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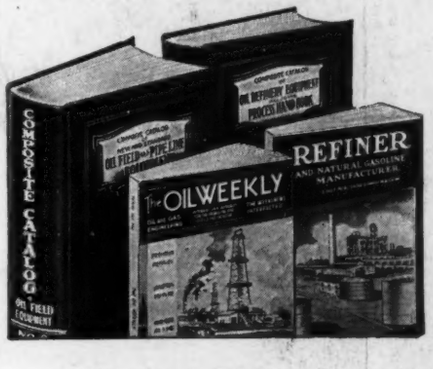

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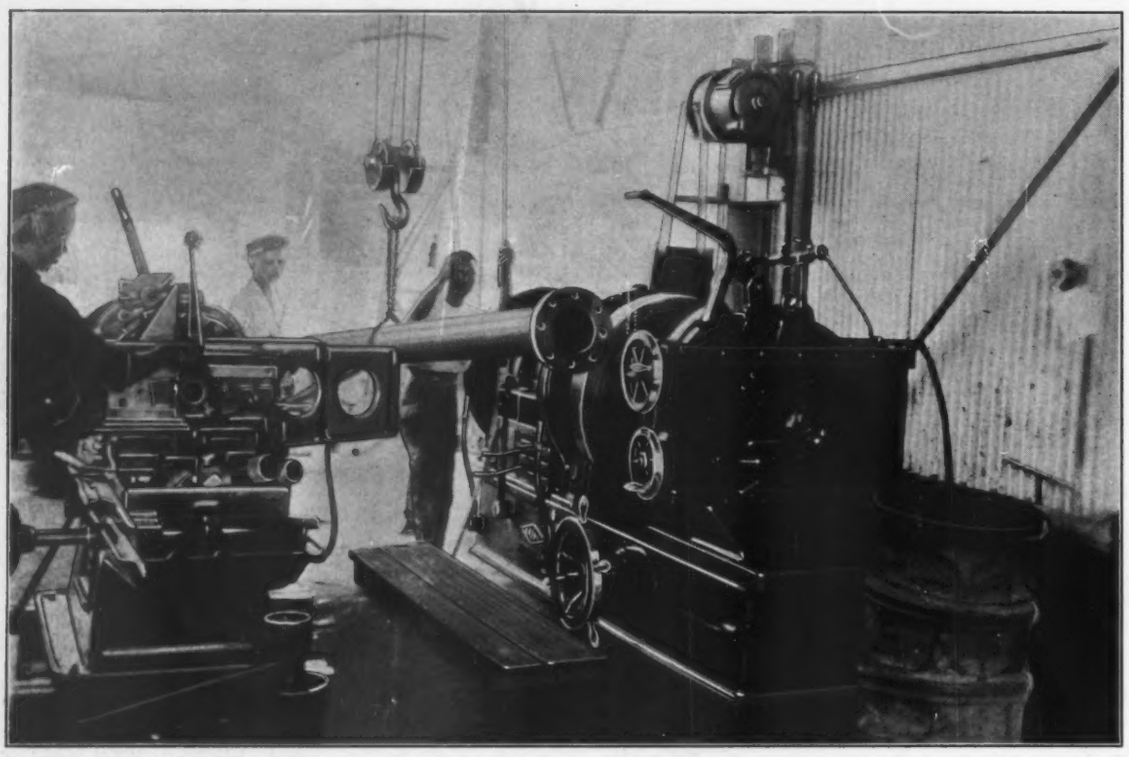

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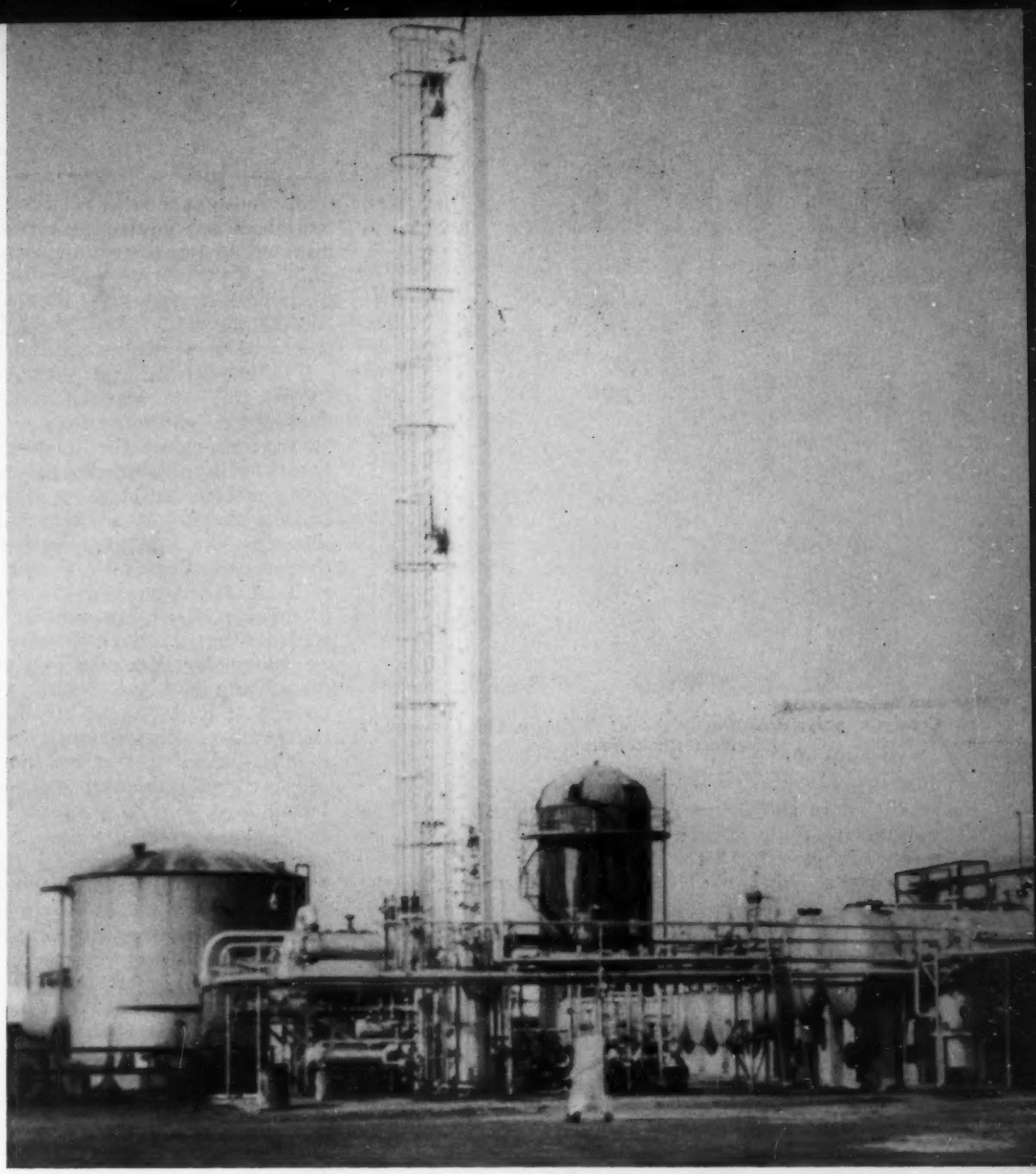


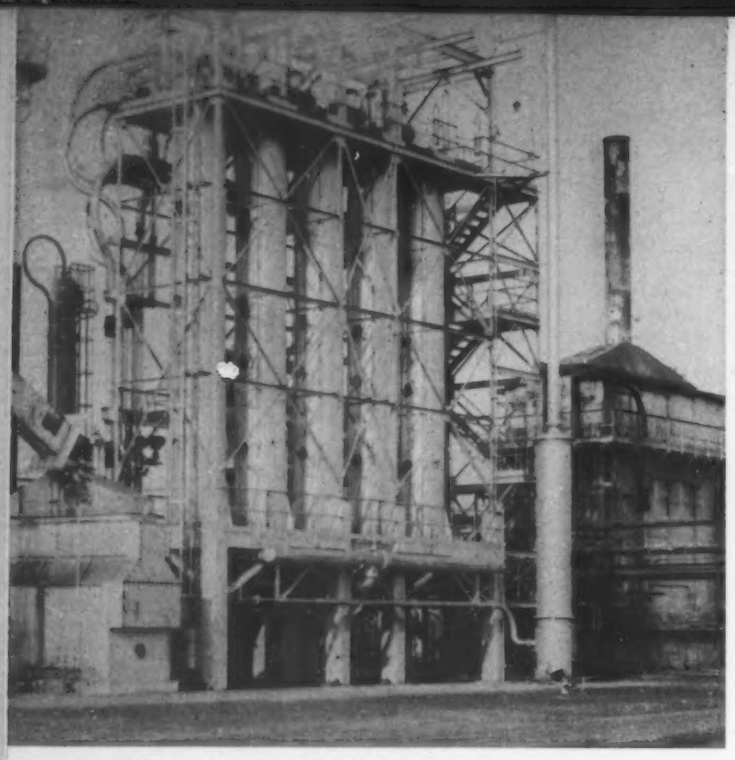
Hydrogen sulfide removal plant used to reduce sulfur content of gases before polymerization. Tripotassium phosphate is used in gas purification.

Gas Purification and Polymerization

AT WILSHIRE REFINERY

JOHN C. ALBRIGHT

AT the time Wilshire Oil Company, Inc., started expanding its refining facilities at Norwalk, California, a plant was designed to process fresh reduced crude. In order to accomplish this, a 15,000-barrel Dubbs cracking plant was constructed together with other units required to finish the products by reducing sulfur and to sweeten for consumption either locally or for export. In the process of cracking fresh or reduced crudes, the gases produced had an olefin content up to almost 36 percent, which, owing to the value of these olefins for blending after suitable processing, was a factor that indicated a polymerization plant would be profitable. Agreement was entered into between Wilshire Oil Company and Universal Oil Products Company for construction of a catalytic polymerization unit, capable of processing the entire gas production of the refinery, plus any gas



Catalytic polymerization plant at Wilshire Oil Company's Norwalk refinery.

produced in the future by reforming naphthas. The polymerization unit was completed in 1937, and, with minor changes, has been operating on refinery gases, showing as high as 98 percent conversion of the olefins to a stable gasoline.

At the time the original combination skimming-and-cracking plant was built, in the summer of 1936, each operation dove-tailed with the other, so that when the cracking plant came down for a clean-out and inspection, all processes, except treating of finished products and subsequent re-running for end-point control, were suspended and no products were manufactured. To insure runs of fresh crude through the refinery, two furnaces were constructed in 1938, one of which is used for skimming the crude, and the other for reforming naphthas; both of which may be operated when the cracking furnaces are being cleaned and inspected, which insures a continuation of refining operations, with the reduced crude subsequently cracked when the main plant is on stream again. Not only does the new arrangement insure continuous operation of the plant, but a yield of 24.6 percent of reformed and light straight-run gasoline can be produced—based on the crude charged to the topping furnace—the combination of which has an octane rating of 72; averaging in quantity of about 160,000 gallons of 380° F. end-point gasoline daily. In reforming the heavy gasoline—or light naphtha—a material increase in unsaturates in the refinery gases provides an increased yield of polymer gasoline in the catalytic plant.

The normal operation of the refinery includes charging of fresh crude to the topping furnace, with light gasoline recovered from overhead vapors and a heavy stream of gasoline, or light naphtha, from the side of the column, and the bottoms from the column are recharged to the Dubbs unit which produces a yield of 32.8 percent cracked gasoline, and a fuel oil of from 7° to 8° API gravity. Gases which constitute the charge to the polymerization plant are produced with a volume of from 1,500,000 to 2,000,000 cubic feet. The gases are gathered from the cracking plant pressure distillate receiver and the reforming process. These gases have an olefin content ranging between 33.3 and 35.7 percent, but also contain hydrogen sulphide in relatively small quantities, but sufficient to require processing before being polymerized. A separate unit, using tri-potassium phosphate as the active agent for removing the sulphur compound, is used. (See REFINER, Vol. 17, No. 6, June, 1938, Page 245, "The Shell Phosphate Process for Removal of Hydrogen Sulfide.")

The charge for the polymerization plant includes vapors from the cracked gasoline stabilizer, which is operated to produce gases rich in saturated fractions so that much of the unsaturates may be removed from the liquid in order that a greater yield of polymer gasoline can be secured. In this type of polymerization plant, only the unsaturates are reacted upon, allowing the saturates, or butanes, to pass through the unit unaffected by the process. These are recovered in subsequent fractionation operations, to be blended in desired proportions with the semi-finished fuels so that the overall octane value may be stepped up materially. Because of the reaction of the polymerization catalyst upon unsaturates only, the recovery of high-octane blending material may be increased by cutting deep in the cracked gasoline when it is stabilized to remove the unsaturates by cutting off a considerable amount of the normal and iso-butanes.

All these gases are handled under pressures commensurate with catalytic polymerization, without requiring the operation of compressors. The gases are delivered as a whole to the H_2S removal plant for conditioning before entering the catalytic gas heater. This plant, a development of Shell Development Corporation, is similar in design and operation to a gas absorption plant containing a vertical column equipped with bubble plates, preheaters, condensers, coolers and a reboiler with a full complement of pumps for circulation of the tri-potassium phosphate solution. The gas enters the base of the column below the bubble plates, and follows the same path as in an absorption column for the extraction of gasoline fractions, becoming intimately mixed progressively with the solution until it is removed from the overhead gas outlet connection, free of the hydrogen sulphide. The tri-potassium phosphate solution is maintained in the system and is recycled over and over, each time being processed through preheaters, a reboiler and coolers, to arrive in an accumulator from which the H_2S is removed and passed through suitable piping to the plant excess gas burning pit, where the hydrogen sulphide is destroyed.

After being processed for the removal of the H_2S, the gas charge enters the polymerization plant heater. Heat is applied to the gas charge to obtain temperatures required for processing through subsequent steps, varying between 380 and 400° F. on the outlet, or transfer line of the gas heater. The gas charge is frequently analyzed for its moisture content so the added amount of water on the furnace inlet may be controlled for optimum operating conditions. The gases from the cracking plant reflux accumulator drum, at the stabilizer unit, ordinarily carry about 1 percent of water vapor, and the gases from the reforming unit carry about .35 percent of water. Cognizance is taken of these percentages so that a proper balance may be maintained without over-saturating the gas with injected water on the inlet of the polymerization gas heater. A small pump is used on the water supply line, being regulated to add a sufficient amount of water to bring the total moisture content

to about 2 percent, which is the volume found necessary to maintain proper hydration of the catalyst.

Five catalyst columns are used in this plant, piped and manifolded so that any number may be operated in series, and so any one of them may be removed from service without disturbing the operation of those remaining. In the normal operating procedure, one of the columns may be off the line while it is being subjected to the process of burning the carbonaceous material from the catalyst and subsequent reactivation with steam. The flow through the catalyst towers is from top to base, in series with the number of towers in service.

The gases leaving the catalyst columns pass through a common header into which dilute caustic soda solution is introduced with a proportioning pump to neutralize the acidity of the subsequent product. While the caustic insures complete neutralization of the gases, it also tends to form a heavy scale in the polymer header with consequent increase in pressure drop to the receiver, seriously affecting the butane yield. This difficulty has recently been overcome by the use of tri-sodium phosphate.

The gas and polymers flowing from the header at the catalyst columns pass through a water-separation drum where a portion of the moisture is condensed and removed, prior to condensing the stable fractions plus the propane and butanes. All products, except the initial deposition of water, flow through a water-cooled condenser to the polymer receiver. This receiver is maintained with a pressure varying from 130 to 175 pounds, depending upon processes employed and results desired, with the hydrocarbons removed by pumping to the depropanizing column. Uncondensed gases are removed from the receiver through an automatic release valve which is connected to piping which leads to the plant fuel lines.

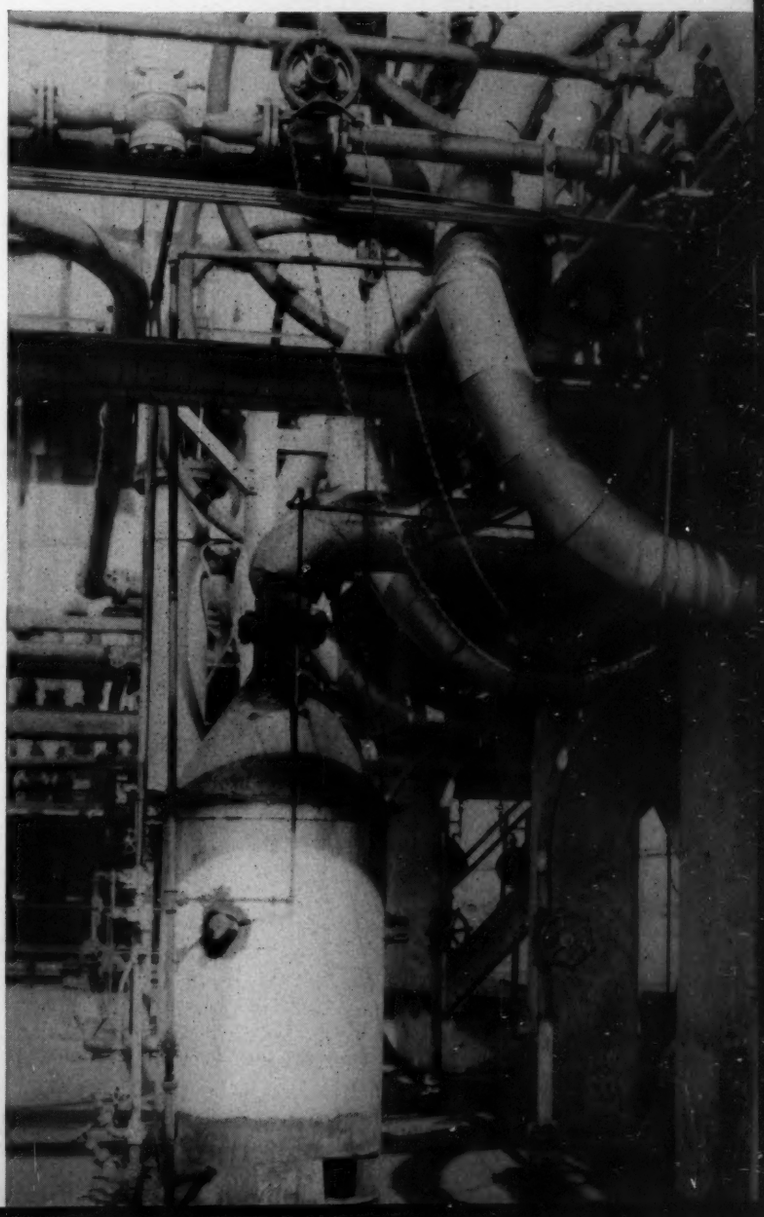
The column at this point is similar in design to any stabilizer tower, but is used to remove only the propane and lighter fractions which may be entrained with the polymer liquid resulting from condensation. The column is equipped with a base reboiler, overhead condenser and accumulator for reflux which is used to control the operation of the column. This is pumped to the top at a ratio of from 1- to 1.75-to-1, based on the feed to the column.

In the original set-up of this plant, it was felt that with the gases removed from the pressure distillate receiver drum, sufficient fractionation could be obtained with only one column. Adequate fractionation could be obtained when the cut of gas to the polymerization plant did not include appreciable amounts of the butanes. Later it was decided that better results could be obtained when larger volumes of gases were charged to the catalyst towers, but, by so doing, valuable butanes were carried along with the butylenes. Consequently, a second column was installed which in effect is a de-butanizing column, serving to recover butanes after depropanizing the raw condensate so these butanes might be used for blending with the various grades of gasoline produced in the refinery.

The new operation takes the bottom product from the depropanizing column, and transfers this material, stripped of the propane, to the debutanizing column while hot from the reboiler, and introduces the liquid at the proper point in the column for subsequent fractionation. The depropanizing column is operated at the required pressure and temperatures, both top and reboiler, to obtain a propane-free liquid, with the uncondensable gases used for fuel or used as a recycle combined with the fresh gas to the polymerization plant. The debutanizer column, identical in construction to the depropanizing column, is operated at the optimum pressure and reboiler temperature to obtain a bottom product with an API gravity of about 67°, a 90° F. initial boiling point, and a 400° F. end-point, having a vapor pressure of 10 pounds Reid. Overhead material is condensed and used as reflux for the debutanizing column at a ratio of 2.5:1, based on the feed, with excess stored and blended with finished gasoline in the proportions for vapor-pressure control and to increase the over-all octane rating of the fuels.

The uncondensed gases derived from the charge to the depropanizing column may either be used as fuel or recycled. The objective obtained in recycling such gases through the catalytic plant is to dilute the olefin content of the fresh gases so that, when a fresh charge of active catalyst is placed in any tower, the active agent is provided with a lean gas with which to wear its "edge" away without over-polymerizing the unsaturates and forming a heavy product which is difficult to use.

In normal operation, the catalytic bed in the columns require regeneration by removing the carbo-



Polymerization catalyst-column jacket-heater in poly plant

TABLE 1

	Total Gas Mcf./ Day	Olefin Content Percent	Average Bbls. per Operating Day	Total Bbls. per 30 Days	Theoretical Bbls. per Operating Day	Percent Olefin Conversion
April	1600	34.4	267	8020	328.9	81.5
May	1554	34.4	304.5	9120	319.4	95
June	1388	35.75	262.5	7890	296.4	89
July	1413	35.6	284.8	8550	300.5	98
August	1429	33.1	254	7650	282.5	90
September	1589	33.37	262	7890	316.8	83
October (10-25-38)	1730	33.5	279	8400	346.1	80.5

naceous film from the grains, and from the minute pores in the grains themselves. In the burning process, oxygen-free flue gas is passed through the bed of catalyst until proper temperatures are established, at which time a controlled amount of oxygen is injected to effect controlled burning. The catalyst columns have a diameter of 36 inches, and an effective bed height of 30 feet, and are jacketed on the outside so the catalyst beds may be heated from outside sources, making it possible to more accurately control the regeneration process. Burning of the bed is begun at 650° F., with the oxygen content controlled and continued at this temperature until the oxygen content reaches a concentration of from 4 to 5 percent. Heating is increased at this point to 750° F., again starting an oxygen-free flue gas. After the oxygen content of the gas has again been built up to the concentration of 4 to 5 percent the process is repeated, but the temperature is increased to an inlet temperature of 800° F. Controlled introduction of oxygen is again used until the bed has been cleaned of its carbon. The total burning-out time on an 800-hour cycle is of the order of 75 hours, and it has been found by experiment that this method produces a more evenly burned and cleaner catalyst than methods formerly used.

The steaming time of the catalyst beds averages 6 hours for each column, with steam introduced at a superheated temperature of 500° F., and with a variable average rate of from 100 to 150 pounds of steam per square foot tower area. The maximum amount of steam does not exceed 300 pounds per square foot, and the minimum does not drop below 75 pounds.

To explain the olefin conversion as shown by the accompanying Table 1, which gives operating conditions from April to October 1938, inclusive, the amount converted in April appears to be exceptionally low. At this time the beds were all filled with fresh catalyst, and the charge gas was diluted with large volumes of gas containing no unsaturates, so that the "edge" as explained elsewhere could be worn off without producing an exceptionally high end-point product. During the succeeding months, the amount of recycle gas was reduced so that a greater conversion was obtained. At the end of October, after more than 2,000,000 gallons of polymer gasoline had been produced, the beds of active material had begun to lose their strength, and, consequently, the conversion rate began to decline.

As a picture of the entire refinery in its operation, the following is given:

With a crude charge of 15,120 barrels per day, the reformer yield, including the light straight-run cut, is 24.6 percent of 72-octane, 380° F.-end-point gasoline —based on the crude charge.

The Dubbs yield from topped crude is 32.8 percent of 69/70 octane, 390° F.-end-point gasoline, having the above octane rating after treating, and a vapor pressure of 7/8 pounds, Reid.

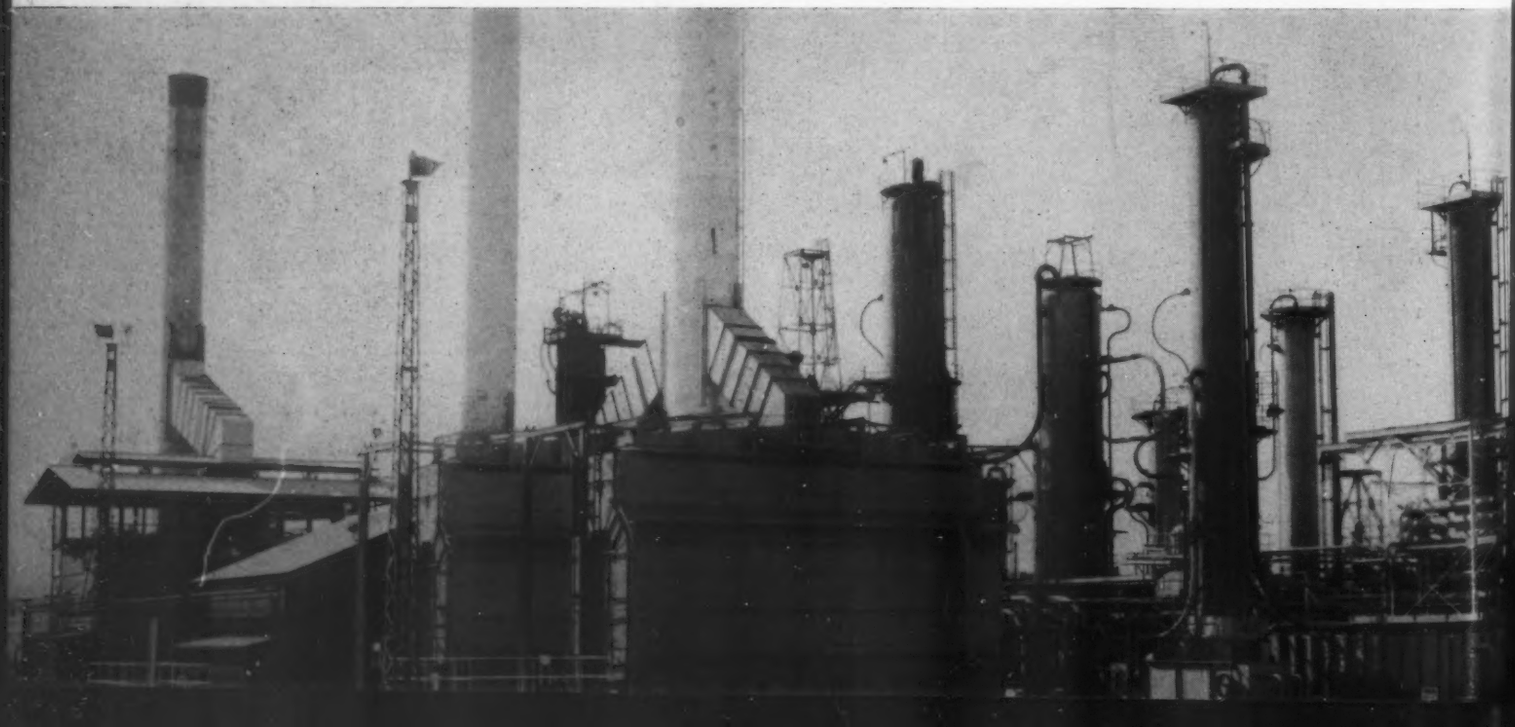
The residue yield from the Dubbs cracking operation is 34.6 percent of 7/8° API, 85 seconds Saybolt Furol at 122° F., and having a 10° F. pour point.

Polymer gasoline by processing 2,000,000 cubic feet of gas at 7 gallons per 1000 cubic feet is 2.22 percent, based on the crude charge.

Excess butane from the polymerization plant, recovered as a liquid product from the overhead condenser of the debutanizer column is .76 percent, based on the crude charge.

In summation, the yields of the plant are as follows:

	Barrels	Percent
Crude charge	15,120	100.00
Reformed products	3,719.52	24.6
Cracked gasoline	4,959.60	32.8
Polymer gasoline	335.664	2.22
Butane	114.912	.76
Fuel oil	5,231.52	34.6
Gas and loss	759.024	5.02
Total	15,120.240	100.00



Dubbs Cracking unit in the background and the new upshot furnaces in the foreground. The nearest furnace is used for reforming naphtha. Gases from these units are polymerized.

RECENT

Filtrol Fractionation Plant *Secures High Efficiency*

M. M. MOORE[1] and H. M. GWYN, JR.[2]

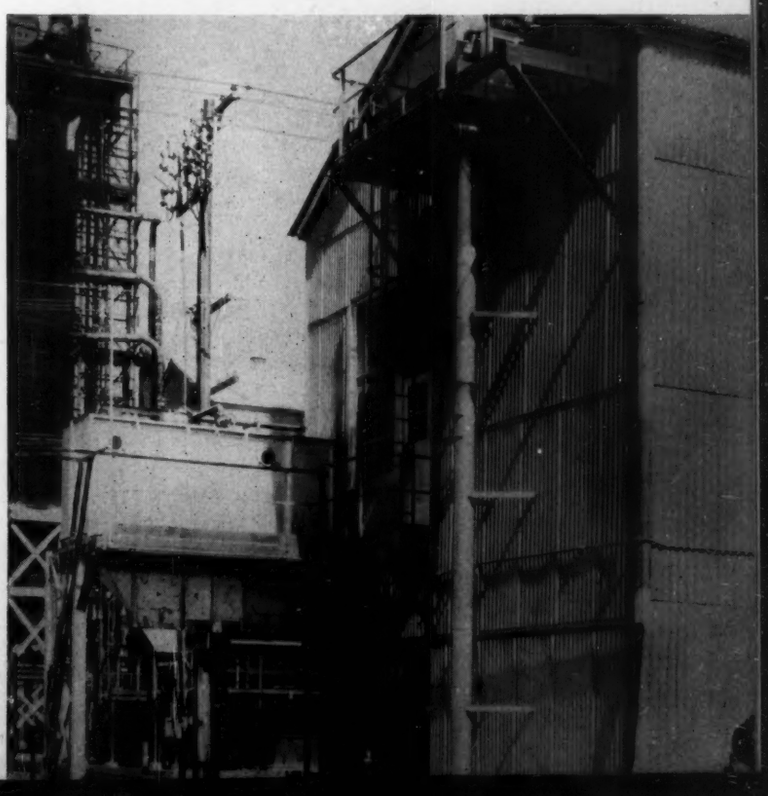
FILTROL FRACTIONATION is the name of the process in which a finely-divided activated bleaching clay is injected into a hydrocarbon oil stream as it flows to some form of fractional-distillation equipment. The purpose of this relatively new technique is to combine fractional distillation and contact-clay decolorization into a single and more economical continuous process. The process has attracted considerable interest for some years, but had not reached its most successful stage of development until it was applied in connection with the vacuum distillation of treated long residuums. Recently Standard Oil Company of California installed a Filtrol Fractionation plant at its Richmond refinery, and it is the purpose of this paper to describe briefly this installation. Factors which made the installation a definite advance in the art of finishing lubricating oils are: careful control of contact time and temperature, steam stripping and continuous filtering of the products, and completely automatic clay handling.

Essentially the Richmond installation (see Figure 1) is a lube oil vacuum re-run unit having those modifications necessary to efficiently employ the bleaching clay in the operation. The plant is capable of charging 1200 barrels a day of solvent-treated long residuum, and the products of the operation are three pale oils and a 5 A.S.T.M. color bright stock, all of which are completely refined products requiring no further treatment. The re-run unit consists of: a heater containing 2¾-inch and 3½-inch O.D. tubing which has a total heating surface of approximately 800 square feet; a 67-foot tower, the upper part of which is 9 feet in diameter and contains 13 bubble plates—the lower section is 5 feet in diameter and serves as a reservoir to permit required contact of oil and clay; heat exchangers; control equipment; pumps; lines and tanks. Other equipment consists of: a 100-ton clay storage bin, automatic clay conveying, proportioning and feeding system; a totally enclosed continuous rotary vacuum filter, the drum of which is 5 feet 3 inches in diameter and 6 feet long, and a vacuum pump.

As indicated in the flow sheet (Figure 2) about 10 percent of the charge to the furnace is continuously by-passed through a 3-foot x 4-foot clay mix tank. This tank is equipped with a mechanical agitator which mixes the clay with the oil, thus forming a readily pumped oil-clay slurry. The clay is automatically fed to this tank by a gravimetric feeder (Figure 3) which is adjusted according to the degree of clay treatment desired. The small clay hopper of this feeding device is kept automatically supplied by a scroll-type conveyor which takes clay from the 100-ton overhead storage bin into which clay is delivered in car lots from a nearby railroad siding by means of a vertical and horizontal unit conveyor. The by-passed oil containing clay rejoins the main flow as it continues on through the overhead, No. 3 cut, and bottoms heat exchangers before entering the furnace. On the present stock a heater outlet temperature of approximately 675° F. is maintained. The oil-clay slurry then enters the vaporizer section of the tower. The operating conditions in this section of the tower are so adjusted that vaporization of the more volatile portions of the charge leaves behind a bottoms product of bright stock viscosity. This unvaporized portion which also contains all of the clay, passes over a number of stripping trays before falling into the soaking section. The lighter cuts thus receive a light clay treatment in passing through the exchangers and furnace and the clay charge is great-

FIGURE 1

General view of the 1200-barrel-per-day plant equipment and clay building and conveyor in foreground. Heater and tower in left background.



[1] Standard Oil Company of California. [2] Filtrol Corporation.

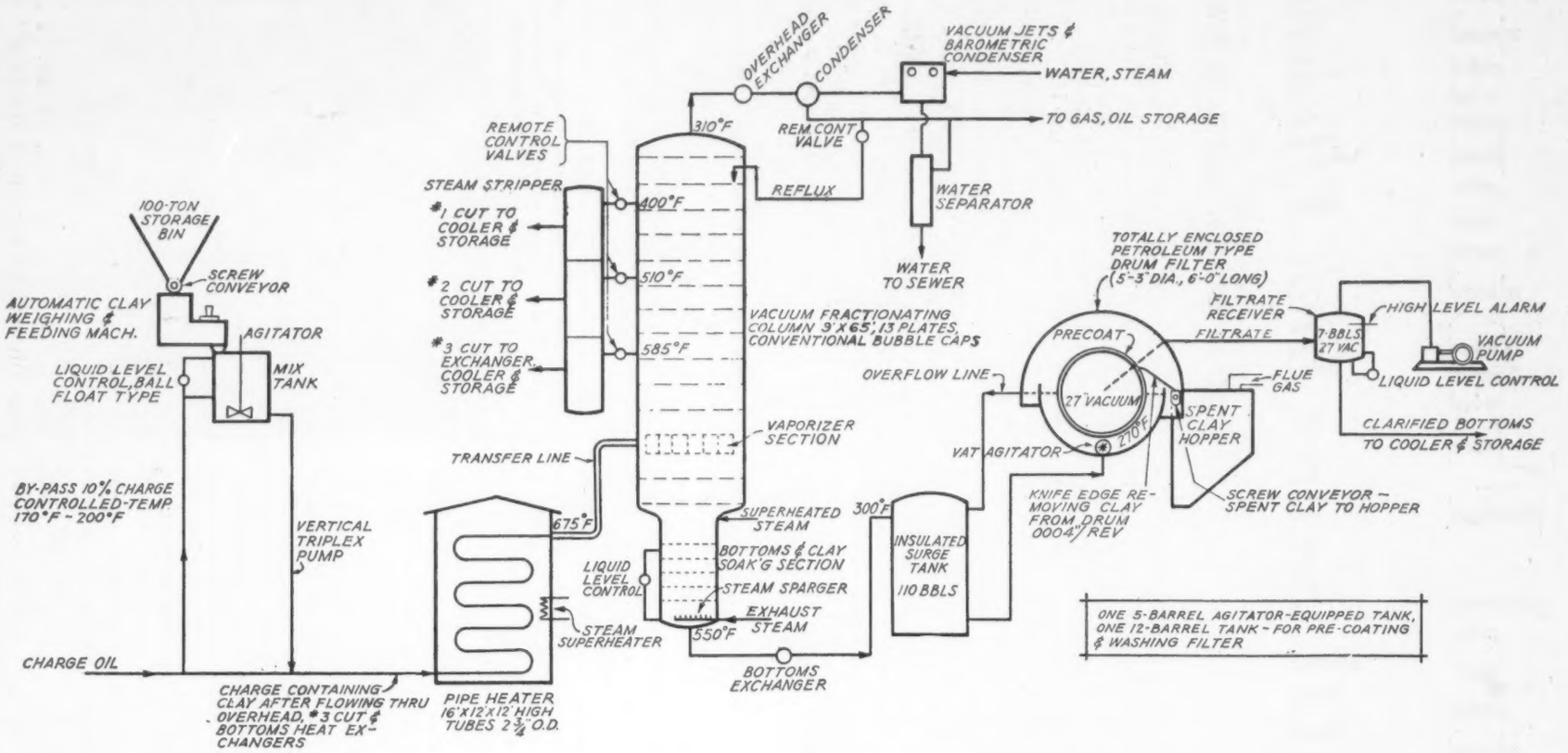


FIGURE 2

Simplified flow of the Filtrol Fractionation plant at Standard Oil Company of California's Richmond refinery.

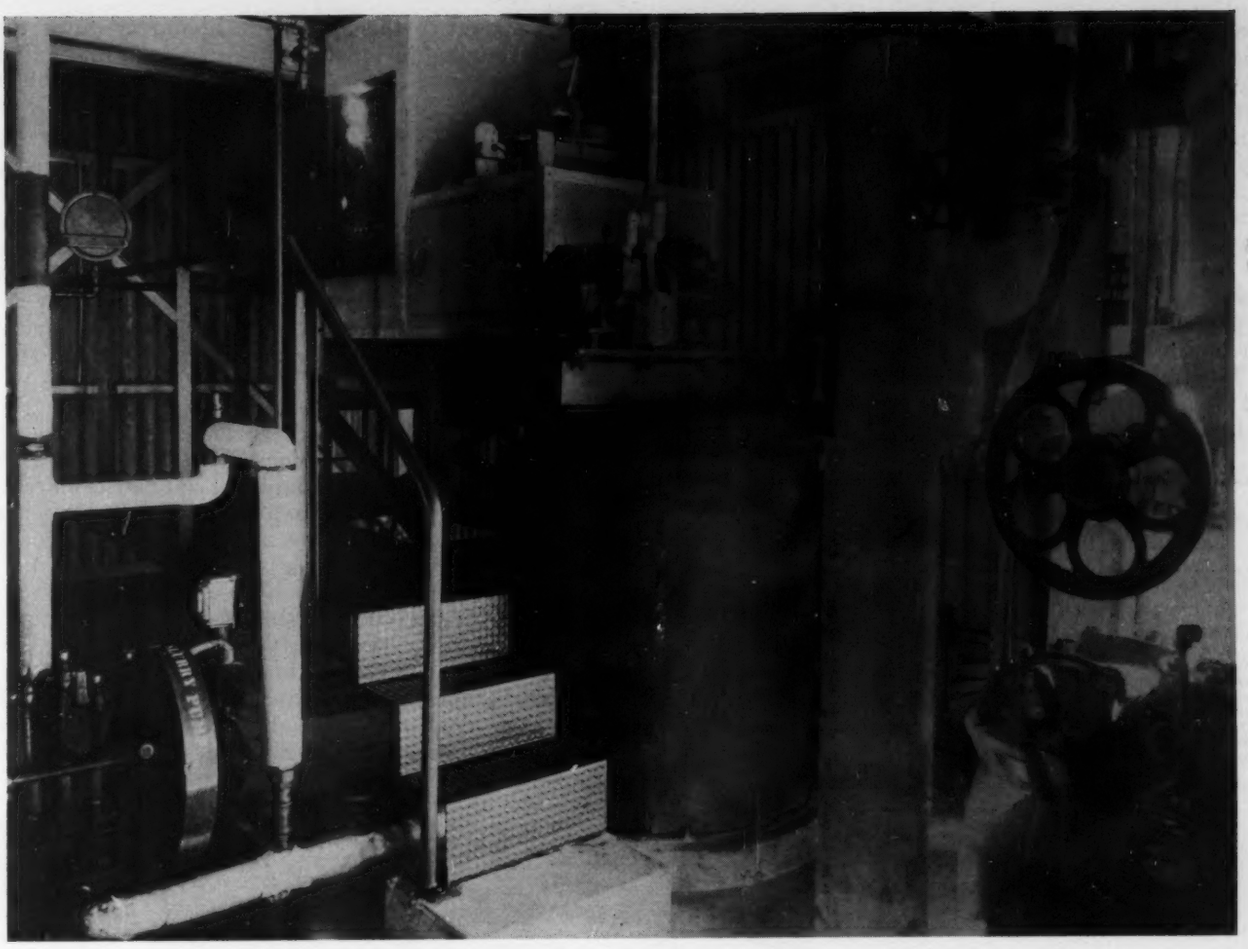


FIGURE 3

Automatic clay weighing, feed, and mixing equipment in background. Part of the vacuum pump in the right foreground.

ly concentrated in the bright stock which requires heavier clay treatment. The vaporized material is fractionated into the three previously mentioned pale oils which are taken off as side streams from the tower. Each cut passes through a steam stripper which eliminates all undesirable odor and insures color-stable products. A small fraction approximating gas oil is refluxed as a means of controlling the temperature at the top of the tower. This reflux, which in the first month of operation amounted to only 2 percent of the charge, is continuously removed from the system. The only other loss of product is the oil which remains in the clay which amounts to less than 1 percent of the oil charged.

The bright stock oil-clay slurry in the soaking section of the tower is agitated and stripped by the exhaust steam injected at the bottom of the vessel through a sparger, or perforated circle of pipe. As the operation is continuous, the contact time is regulated by automatically controlling the liquid level of the oil. Fifteen to 20 minutes has given satisfactory results thus far. The slurry then passes through the bottoms exchanger and into an insulated surge tank from which the continuous filter is fed. Slow pump circulation is maintained on this tank to prevent the clay from settling to the bottom.

The continuous vacuum rotary drum filter used (Figure 4) represents a relatively new development in fine clay filtration plants. The Monel metal cloth which forms the drum's surface is first pre-coated with a three-inch layer of diatomaceous earth. It is this coating which performs the filtration, the clay being retained on the surface. The pre-coating operation is accomplished by circulating a small quantity of a light oil from a 4- x 6-foot tank equipped with a mechanical agitator, to the vat of the filter in which the drum revolves, through the drum and back to the tank. The diatomaceous earth is gradually fed to the pre-coat mixing tank and as circulation continues the earth is deposited on the filter drum. Vacuum is maintained on the drum by means of a motor-driven pump. The oil level in the filtrate-receiving tank is controlled automatically at approximately 1 foot, thus preventing oil from being drawn into the vacuum pump. The pre-coating operation is required but once a week and takes about 3 hours. As soon as the desired thickness of pre-coat has been applied, the filter is charged with bright stock containing clay from the surge tank. Filtration is continuous, a finished bright stock being produced. As the filter drum revolves picking up the spent clay and allowing the oil to filter through and pass to storage, a knife edge moves in against the pre-coat. This strips off the clay and cuts off the pre-coat at the rate of .0004 inches per revolution. The drum has an area of 100 square feet, and operating at 300° F., has successfully filtered 500 barrels of the bright stock per day. This figure, however, does not represent the capacity of the filter since it can be increased considerably by speeding up the rotation of the drum, increasing

the pre-coat cut or raising the temperature of operation. The filter is equipped with a spray system for washing off the last trace of pre-coat before beginning another cycle. The clay is prevented from settling out in the bottom of the filter vat by a paddle agitator. The spent clay and pre-coat material from the knife edge is continuously removed by a scroll conveyor which empties into a hopper. The rerun, clay contacting and filtration equipment is operated by two men per shift, one of whom is assigned to the distillation equipment. The operating costs show the expected saving as compared to the cost of separate rerunning and filtration by contact or other means.

The following are typical of results obtained, when clay was being added at the rate of 0.125 pounds per gallon of charge.

	Charge Oil	No. 1 Cut	No. 2 Cut	No. 3 Cut	Bottoms	Overhead Slop or Gas Oil Cut
Gravity, A.P.I.	28.9	33.9	31.4	31.1	27.2	31.1
Flash C.O.C.	435	350	405	485	595	220
Vis. S.S.U. at 100° F.	400	75	174	421	2615	46
Vis. S.S.U. at 210° F.	58.1	37.3	44.6	59.3	151	...
Vis. Index	98	.....	95	98	93	...
Color A.S.T.M.	4	1	1	1½	5	...
Color Hold (After 16 hours at 210° F.)	.....	1½	1½	1¾	6	...
Pour	+10	+10	+10	0	0	...
Carbon Residue	.08	0	0	.01	.30	...
Neut. Number	.10	.03	.03	.03	.03	...
Yields, percent	100	5	25	43	25	2

In addition to the above the bloom or outer tone of each finished product is of a very desirable nature. The bright stock in particular has a good velvety green color when seen by reflected light.

It may be of further interest to pount out that Filtrol Fractionation can also be used to advantage in a number of other stages of lubricating oil refining. For example, it can be employed on solvent mixtures of lubricating oils which have been made up to facilitate other refining steps, as in the case of naphtha solutions prepared in connection with centrifuge de-waxing. In this instance, after centrifuging, conventional practice calls for a naphtha stripping operation followed by decolorization with bleaching earth. By employing the Filtrol Fractionation principle, both of these latter operations can be accomplished simultaneously. Again, crude oils containing but small amounts of asphaltic material, and those in which the asphaltic content has been materially reduced, can be refined by this process. Such units produce better quality naphthas, kerosenes and intermediate fractions, in addition to finished lubricating cuts of the desired color. Sour or neutralized long residuums which are being subjected to vacuum distillation and clay finishing appear to be another phase where this process can be profitably employed. No doubt other applications will occur to readers familiar with the detailed refining steps of individual plants.

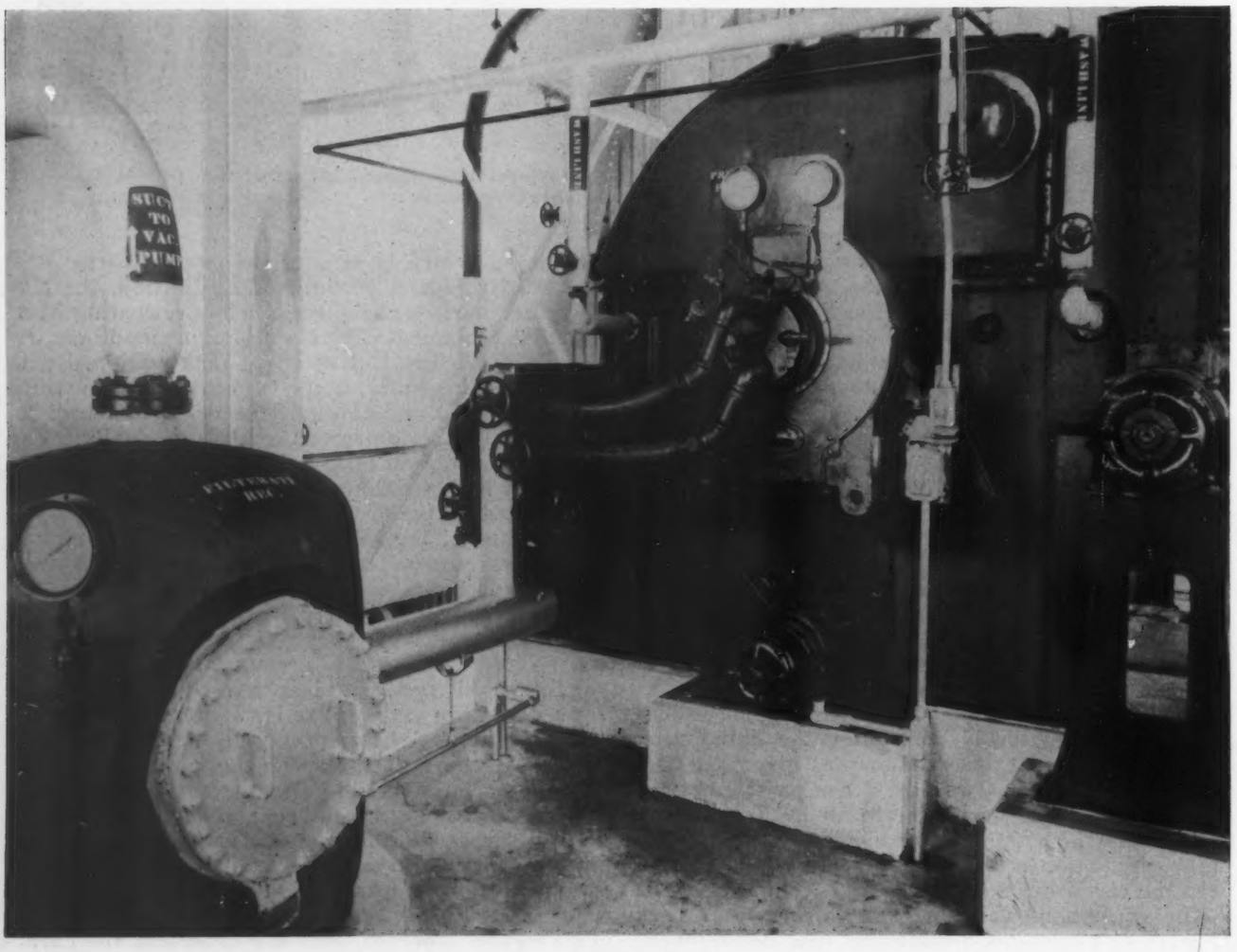


FIGURE 4

Continuous vacuum filter and filtrate receiver. Clay storage bin in the background

New Design Features

In Small Combination Unit

JOHN C. ALBRIGHT

AFTER acquiring a small skimming unit at Leuders, Texas, near the recently discovered Avoca oil field in northeastern Jones County, Panhandle Refining Company decided that the unit could be inexpensively converted into a modern combination skimming and cracking plant to produce a high-octane gasoline. The original plant was built several years ago, and had been operated to produce a straight-run gasoline, with other overhead products, and disposing of the residuum as fuel oil.

Under the direction of W. F. Sims, manager of refineries, the company worked out a design which included skimming the fresh crude by exchanger heat without a pipe still, and using only one furnace to contain heating coils for cracking both the light and heavy charges of oil. The overall capacity of this plant is reckoned in barrels of oil as charged to the skimming unit, and has a nominal capacity of approximately 1050 barrels a day. Efficient operation has stepped up throughput to an average of 1400 barrels of 37-gravity crude a day, without changing the fundamental design of the plant in any manner and with a fuel consumption of only 1.7 percent, calculated on the amount of crude charged to the unit.

Most of the equipment originally employed in the operation of the first plant is no longer in use, and practically all of the equipment required to build the new plant as it is now being run was purchased new, with columns and towers built to order. The cracking side of the plant is operated under license from Universal Oil Products Company, who accepted the design. The furnace of this plant is a small edition of the conventional two-coil heater, up-shot firing and counter-flow. One side of the furnace is used for processing the heavy oil obtained from the base of the main fractionating column. The other side processes the customary light oil charge obtained from a mid-section draw-off on the same tower.

The hot oil pump was designed especially for this cracking plant, and was built with a steel billet body

Panhandle Refining Company's Leuders combination plant. Boilers at right, heat exchange skimming, right center, cracking plant at left. Looking directly south into plant yard from paved highway.

and stainless steel water-cooled, outside-packed plungers, and is driven by a vertical, single-cylinder steam engine, directly connected by a flexible coupling. The plungers of this pump are of unequal size; the hot oil plunger being 4½ inches with a 12-inch stroke, and the light oil side having a bore of 3½-inches, with a 12-inch stroke. The fundamental plan of this pump follows that employed when building the larger conventional units, with the same type bed-plate and crank-shaft. The speed of one piston is the same as the other, which, under ordinary circumstances would indicate that the pump might run "lop-sided" or with a jerky, uneven motion. The opposite is the case, however, as the difference between the pressure on either side compensates for the difference in the bore and volume handled. As the heavy oil leaves the larger piston at 390 pounds gauge, and the light oil leaves the other at 420 pounds discharge pressure, the pump operates as smoothly as it would be if the bore of each side were the same and each cylinder was handling the same material at equal discharge pressures.

The crude oil produced from fields close to the plant has a gravity of about 37.1° A.P.I., and can be processed down to an average of about 20 percent of its original volume as bunker C. fuel oil. The remainder of the crude, when processed, is recovered as straight-run products, cracked gasoline and uncondensable gases.

The usual type of steam-driven reciprocating-plunger pumps are used in the plant to handle the fresh crude and products of the refinery. One of these units is used to pump the fresh crude to the crude distillation section of the plant, which uses only exchanger heat to obtain the required temperatures for separation of the various straight-run fractions from the charge. The crude-charge pump operates at a predetermined speed, holding the volume of oil for processing to an average of about 58 barrels per hour, which is directed to the three horizontal, shell-and-tube heat exchangers, operated in series so far as the charge of fresh crude is concerned, to obtain the temperatures for adequate skimming.

The pressure on the charge of crude directed to the exchangers is held at 32 pounds, and under this pressure, the oil travel through the exchangers, the salt settling drum and the skimming tower without further pumping. The first exchanger in this series is located at the top of the stacked units, obtaining its exchange of heat from the straight-run vapors removed from the top of the skimming column, which averages about 180°F. The next exchange of heat is obtained from a side cut of oil taken from the main fractionating column in the cracking plant, at the draw-off point where the light oil is removed for cracking. The volume required to raise the temperature of the oil from 180°F. to 350°F. at the outlet of the second exchanger is 18 gallons per minute.

The oil is taken from the outlet of the second exchanger and fed to a settling drum where all foreign matter is removed prior to its return to the exchanger heating elements to prevent chloride corrosion in subsequent units, and to prevent mechanical stoppage of cracking tubes and vessel outlets by precipitated salts. Returning to the heat exchanger bank, the oil is raised in temperature with a stream of oil taken from the base of the main fractionating column at a rate of 30 gallons per minute to an average of 520°F. when it enters the fractionating column for separation of the required cuts as overhead and side products.

The products obtained with this system of primary distillation are gasoline, kerosene, distillate, tractor fuel and topped crude. At times, it is desired to obtain U. G. I. gas oils, which changes the method of fractionation slightly, with this product recovered having a gravity of around 38° A.P.I. The gasoline recovered as an overhead product has the following characteristics:

STRAIGHT-RUN GASOLINE

Initial boiling point	120°F.
5 percent over	167°F.
10 percent over	192°F.
20 percent over	220°F.
30 percent over	236°F.
40 percent over	256°F.
50 percent over	276°F.
60 percent over	294°F.
70 percent over	312°F.
80 percent over	336°F.
90 percent over	363°F.
95 percent over	396°F.
End Point	423°F.
Recovery, percent	97
Gravity	59.3° A.P.I.

A typical distillation of the gas oil is as follows:

GAS OIL

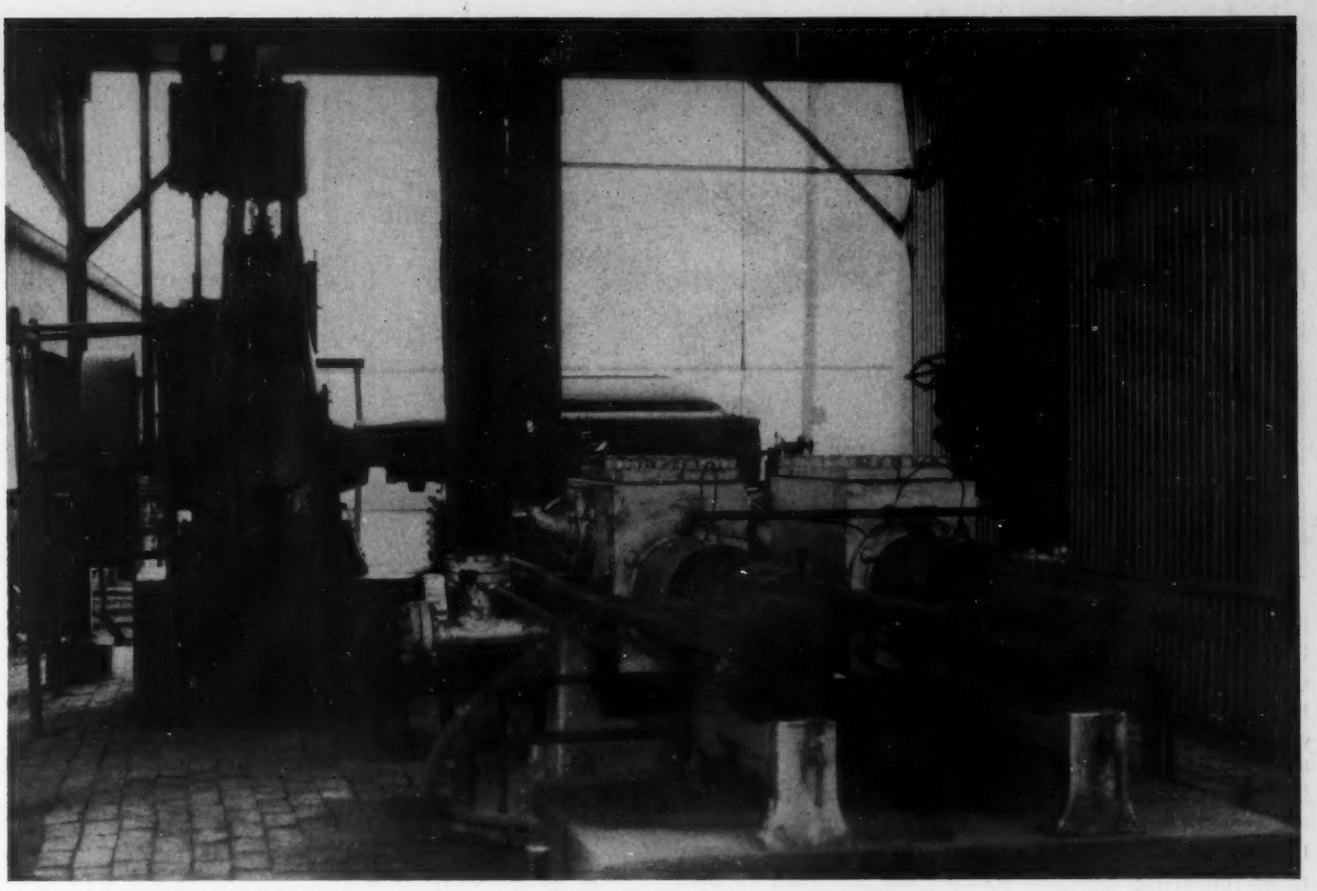
Initial Boiling Point	360°F.
5 percent over	450°F
10 percent over	485°F.
20 percent over	520°F.
30 percent over	537°F.
40 percent over	550°F.
50 percent over	560°F.
60 percent over	570°F.
70 percent over	580°F.
80 percent over	594°F.
90 percent over	624°F.
95 percent over	656°F.
End Point	686°F.
Gravity	37.5° A.P.I.
Color	Light Straw
Distillation recovery, percent	98

When kerosene is produced and stripped in the side stripper, the distillation is as follows:

KEROSENE

Initial Boiling Point	390°F.
5 percent over	402°F.
10 percent over	412°F.
20 percent over	420°F.
30 percent over	428°F.
40 percent over	436°F.
50 percent over	444°F.
60 percent over	454°F.
70 percent over	464°F.
80 percent over	476°F.
90 percent over	492°F.
95 percent over	506°F.
End Point	522°F.
Gravity	42.8° A.P.I.
Color	25
Doctor	O. K.
Corrosion	O. K.
Distillation recovery, percent	98

With the above products removed from the crude charge, the bottoms, around 25.5° A.P.I., are pumped to the main fractionating column of the cracking plant at a temperature of 465°F. and having a volume



Steam-engine-driven hot oil pump. Pump has two sizes of plungers, operating at different pressures. One plunger is used for heavy oil and the other for light oil charge to cracking still.

of from 600 to 650 barrels per day, leaving the raw-oil pump at a pressure of 85 pounds, gauge. Suction is taken from the base of the main column with the larger of the two plungers of the hot-oil pump and delivered direct to the heavy-oil side of the cracking furnace. The gravity of the heavy-oil charge averages between 20 and 21 A.P.I. gravity, and is processed in the heavy oil side of the heater with a pump discharge pressure of 390 pounds, and heated to a temperature of 905°F. at the furnace transfer line. Light oil for cracking in the other side of the furnace has a gravity of around 30° A.P.I. and is handled by the small-bore side of the hot-oil pump, having a suction temperature of about 600°F. The pressure on the discharge of this material is held at 420 pounds, and it is heated in the light-oil side of the heater to 1010°F. in the transfer line.

The flow through the plant from this point is conventional, with the two streams from the furnace entering a common reaction chamber, carried at 885° F. and at a pressure of 260 pounds, gauge. Materials are released from the reaction chamber through a slide valve controlled from the pump room, with cracking arrested by a low-pressure stream of oil from the fractionating column. The flash chamber is operated at 80 pounds and carries a temperature of 870°F. Vapors are directed to the main fractionating column, while residuum withdrawn from the flash chamber constitutes the fuel oil produced. A typical fuel oil in tank car after loading is shown below:

FUEL OIL

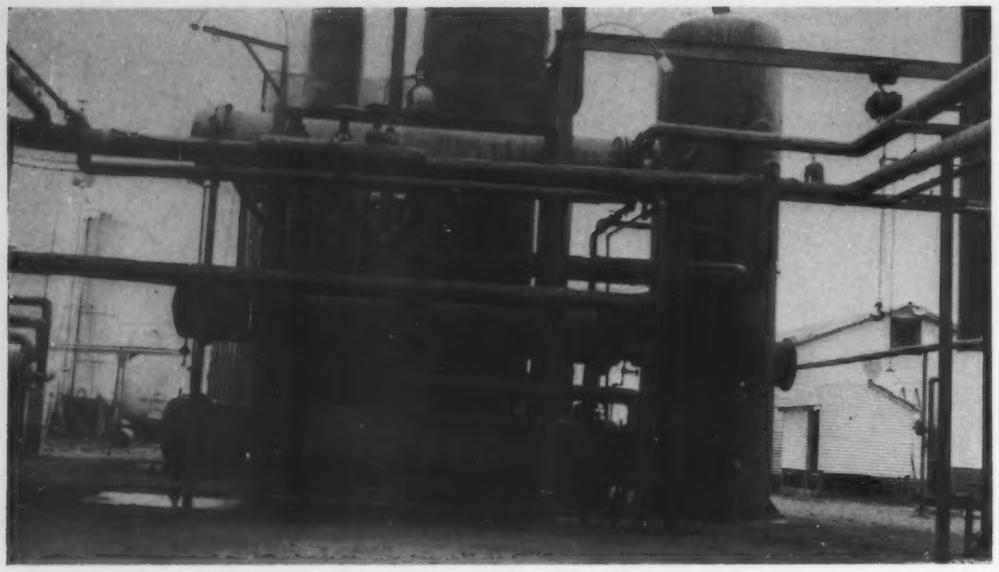
Gravity	7.3° A.P.I.
Flash (O.C.)	195°F.
Fire	295°F.
Furol Vis @ 122°F.	237 seconds
B. S. & W.	.4 percent

The fractionating column is operated at a pressure of 75 pounds and an overhead temperature of 330°F. with pumped reflux to obtain a finished pressure distillate as shown below:

PRESSURE DISTILLATE

Gravity	59.8° A.P.I.
Initial Boiling Point	80°F.
5 percent over	106°F.
10 percent over	124°F.
20 percent over	158°F.
23 percent over	167°F.
30 percent over	190°F.
40 percent over	220°F.
50 percent over	246°F.
60 percent over	272°F.
70 percent over	298°F.
80 percent over	326°F.
90 percent over	356°F.
95 percent over	380°F.
End Point	396°F.
Recovery	96%
Octane value	71
Reid vapor pressure, pounds	7-8
Doctor	O. K.
Corrosion	O. K.

This plant is fully equipped to stabilize pressure



Heating exchangers in Panhandle Refining Company's plant at Leuders, Texas, which are used to effect skimming of crude with heat from plant instead of the use of a pipe still.

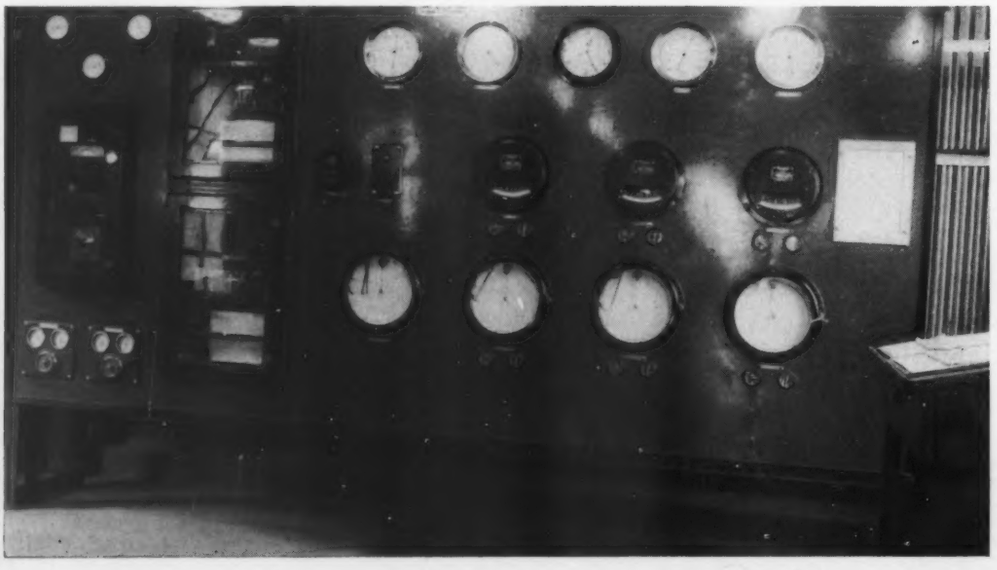
distillate and to process uncondensed vapors from the pressure distillate accumulator drum. The reflux drum pressure is maintained sufficiently high that the vapors will be forced through the absorber without compression. At 75 pounds gauge, these vapors are piped to the combination column which serves both as a stabilizer for the pressure distillate, and as an absorber of the vapors. The column is in effect two towers, one superimposed upon the other, with gases entering the top section for absorption, and pressure distillate pumped to the lower section for reduction in vapor pressure. Vapors from the pressure distillate can pass through a vent from the lower to the upper, and absorption medium may travel through a down-comer from the upper to the lower section. During normal operation, when charging 1400 barrels of fresh crude to the plant, and producing 52.6 percent of pressure distillate from the cracking charge, it is required that about 4.3 gallons per minute of naphtha be pumped to the absorber to strip the uncondensed vapors.

A resume of the operation of the plant is as follows:

Commodity	Percent	Barrels
Crude charged to skimmer	100	1,400
S. R. gasoline produced	31.9	446.6
Kerosene	12.0	168.0
Distillate	3.1	43.4
Diesel fuel	2.6	36.4
Fuel oil (based on crude)	19.8	277.2
P.D. (based on crude)	27.5	355.0
Gas and loss	3.1	43.4
Total	100.0	1,400.0

The cracking plant produced, when based on cracking stock charge, a percentage conversion of 54.3. It is calculated that the fuel requirements of this plant averages about 1.7 percent of the crude charged to the plant, which indicates that only 23.8 barrels of fuel oil would be necessary to maintain the temperatures for adequate refining of Jones County crude. Gas is used as fuel in the cracking furnace, except when the plant is being brought on stream, and excess gas recovered from the absorption plant is used in the water-tube boiler which furnished steam for pumps and other operations in the refinery.

The cost of erecting this plant was less than $90,000, which indicates that the cost per barrel, based on crude charge was around $64.



Recorders, flow controllers and other controls on panel board in control room.

Determination of Gum in Oils Heavier Than Kerosene

F. L. SMITH and E. B. SHANNON

Skelly Oil Company Laboratories, El Dorado, Kansas

THE need for some method of determining comparative gum contents of oils too heavy for analysis by the air-jet method (A.S.T.M. Designation D381-34T) has been felt in this laboratory for some time. Since the gums present in petroleum oils are usually very soluble in ethyl alcohol it was decided to experiment with this method.

While this method does not give the same results as obtained in other currently used methods, it does give excellent information for comparing the gum contents of different heavy oils. In order to check our results, determinations were run on samples which could also be checked by the air-jet method. In every case, the results by the extraction method were much lower than those by the air-jet method; however, they were of good comparative value; that is, those giving high air-jet results gave high extraction results and vice versa.

TABLE 1

Sample No.	Gum, Air-Jet	Gum, Extraction
11740	18.9 mgs./100 ml.	8.4 mgs./100 ml.
11742	15.9 mgs./100 ml.	6.5 mgs./100 ml.
11750	28.2 mgs./100 ml.	15.25 mgs./100 ml.

From Table I, it is seen that the extraction method gives good comparative results and is especially applicable to products on which no other present method will work.

PROCEDURE

One hundred ml. of oil and 50 ml. of 80° petroleum naphtha are accurately measured in to a 500-ml. separatory funnel and 20 ml. of absolute ethyl alcohol are added. The funnel is shaken vigorously for about 30 seconds and 10 ml. of distilled water added and shaken with a swirling motion. Allow the emulsion to break and drain the alcohol-water layer into a clean beaker. If trouble is encountered in breaking the emulsion another 5 ml. portion of water may be added. Remove as much of the water-alcohol solution as possible before proceeding with the second extraction.

Repeat the extraction as described above twice more and after the third extraction wash with an extra 10 ml. portion of water to remove any last traces of alcohol from the oil.

Discard the oil and wash the alcohol-water extract with 2 or 3 portions of 80° petroleum naphtha to remove any oil which may have carried over. Evaporate the extract in a weighed glass evaporating dish on a steam bath and heat in a constant temperature oven at 212° F. to 220° F. for 12 hours. Cool in a desiccator and reweigh.

DISCUSSION OF PROCEDURE

The light petroleum naphtha is added to lower the specific gravity of the oil in order to make the difference in weights of the oil and alcohol-water solution great enough to facilitate breaking the emulsion. While some oils may be sufficiently light that this is not necessary, it is best (to standardize the procedure) to add it in every case.

The procedure was tried with 95 percent alcohol and with alcohol denatured with Formula 3A and was found unsatisfactory in both cases since it was impossible to obtain a good extraction owing to the degree of immiscibility of the impure alcohol with the oils.

With ordinary analytical precautions, in almost every case this method yields results which check within less than a milligram. Table II gives results from a number of samples run in this laboratory.

TABLE 2

Sample No.	A.P.I. Gravity	Gum by Extraction in Mgs./100 Ml.		
		Run 1	Run 2	Average
1	31.8	9.6	11.0	10.20
2	....	12.7	13.0	12.85
3	34.4	10.0	9.6	9.80
4	35.0	20.0	20.0	20.00
5	....	9.5	10.4	9.95
6	37.7	6.7	7.0	6.85
7	35.3	62.8	63.7	63.25
8	35.0	83.1	82.7	82.90
9	36.3	6.1	6.2	6.15
10	34.9	7.5	7.3	7.4
11	34.7	10.6	10.0	10.3
12	35.8	6.7	6.5	6.60

Shell Operates First California Furfural Plant

SHELL OIL COMPANY began operating its new furfural refining process at Martinez, California, during the summer of 1938. The plant is used for refining lubricating oil distillates from various San Joaquin Valley crudes. The solvent furfural is employed to selectively dissolve and remove the undesirable asphaltic and naphthenic constituents in the raw distillate charged to the plant. The unit has a charging capacity of from 2000 to 4000 barrels per day of distillate, depending upon the degree of refinement required and the solvent ratio employed. It is possible to produce lubricating oil of highest quality by such solvent methods.

The furfural refining process was developed and is licensed by The Texaco Development Company and the Shell plant is the first of this type to be erected in California and is one of the largest solvent type installations on the Pacific Coast. This plant was designed by The Lummus Company and erected in about seven months. In the general view, Figure 1, the heater for vaporizing the furfural from the extract and raffinate solutions is shown at the right. The distillation equipment is located in the foreground. The higher tower near the center is a continuous counter-current extraction column in which the undesirable constituents are seperated continuously from the desired raffinate. Furfural storage tanks are located to the rear of the distillation equipment and just below the large storage tank in the background. Rundown tanks are shown at the left of the fractionating equipment. All of the pumps are located beneath a concrete shelter between the fractionating column and the extractor tower.

Figure 2 shows the pump and piping installation for operation of the system. All pumps are located convenient to the fractionating towers. Motor-driven centrifugal and direct-acting steam pumps are used, depending upon the various services. A reciprocating vacuum pump is supplied for maintaining a vacuum on the extract and raffinate stripping towers. The piping in the pump-room is overhead and a liberal amount of clearance is provided. No lines obstruct passageways and all of the pumps are readily accessible for maintenance work.

The heater, shown in Figure 3, is a multi-chamber-type heater in which the furfural is vaporized from the extract in one chamber and from the raffinate in the other. The hot flue gases from the raffinate section pass into a plenum chamber, where they join the flue gases from the extract section. Together they pass through the convection section of the heater. The convection heat is absorbed by the extract solution prior to entering the radiant section of the extract coil. The heater is of the suspended wall construction, the walls being made up of light-weight, super-refractory insulating fire brick. Both chambers of the heater are fired with gas, using floor burners, which may be adjusted from the manifold in front of the heater and controlled as a unit from the control room board or from the fuel header leading to each chamber. The heater is steel enclosed and consequently there is a minimum of air infiltration.

FIGURE 1

General view, Shell Oil Company's new Furfural refining plant at Martinez, California.

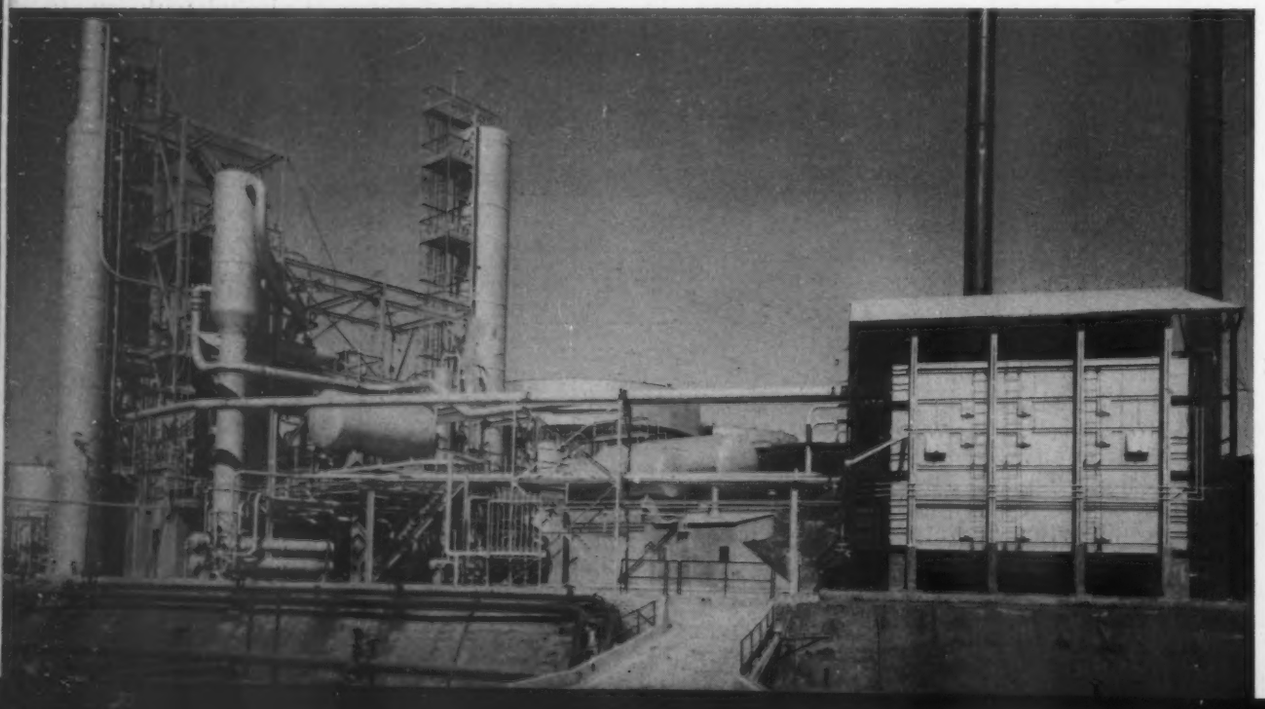
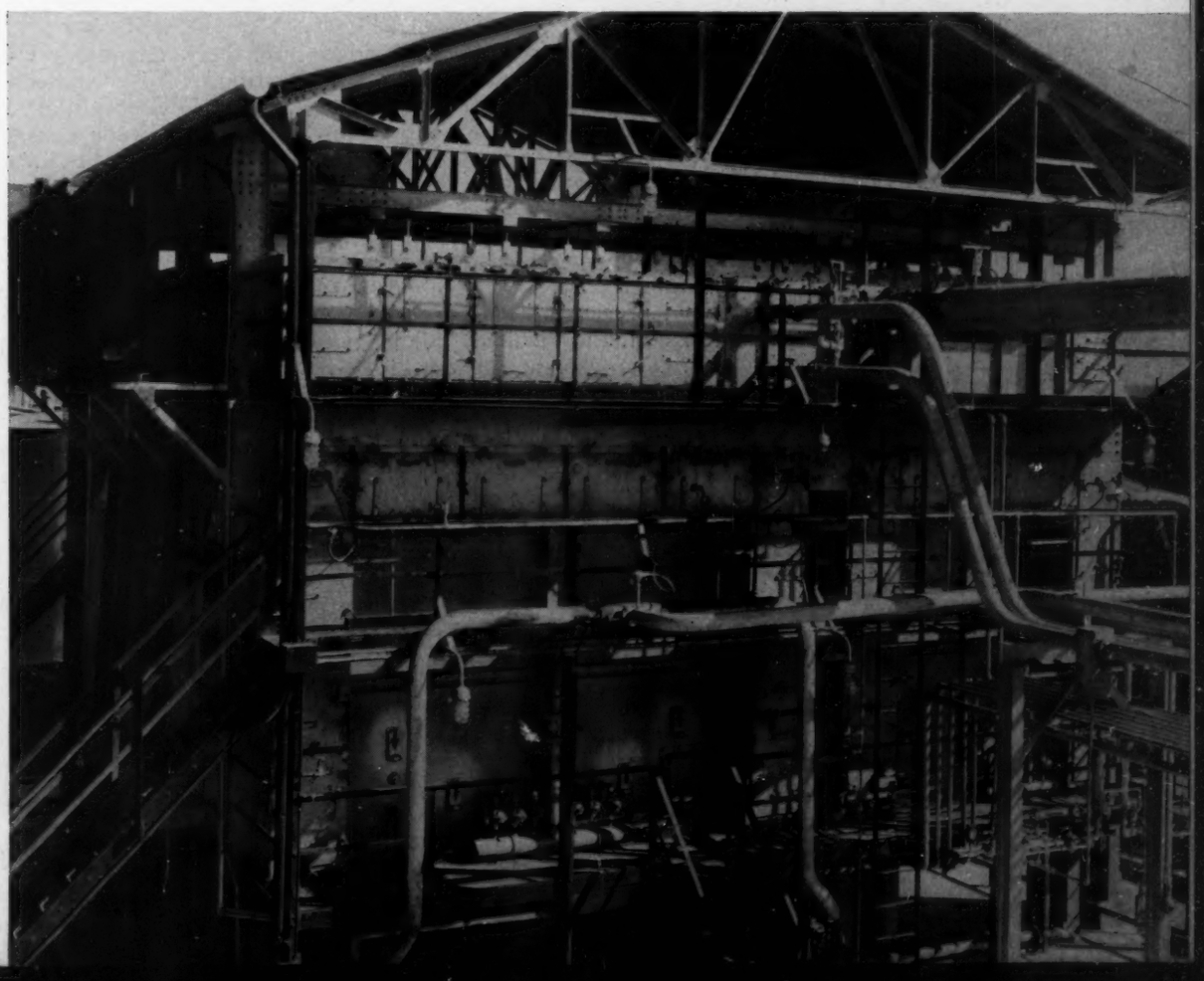


FIGURE 2

Process Pumps are located beneath a concrete platform convenient to the fractionating equipment.

FIGURE 3

Details of the Heater construction are shown



Modern Design in 14,000 Barrel Cracking Unit

GENERAL PETROLEUM CORPORATION'S new cracking plant, representing an investment of about one million dollars, at Torrance, California, started operating during the late summer of 1938. The cracking unit is designed for charging 14,000 barrels per day of 16.5-gravity A.P.I. mixed reduced crudes. The unit is equipped with a multi-chamber cracking heater, one section of which is employed for cracking reduced crude once through, subsequent to the removal of a straight-run gas oil fraction, and another section is employed for cracking the heavy-cycle gas oil. The unit normally operates for the production of stabilized pressure distillate, straight-run gas oil, cracked gas oil, and finished fuel oil of 125 seconds viscosity. The charge for which the plant was designed is of 80°F. pour point and the finished fuel oil has a pour point of approximately 20°F. The wax in the residue is almost completely removed in a vacuum fuel oil flash tower and is then cracked in the cycle gas oil coil. The unit was designed, and erected by The Lummus Company in about eight months. Three operators per shift are required for this plant.

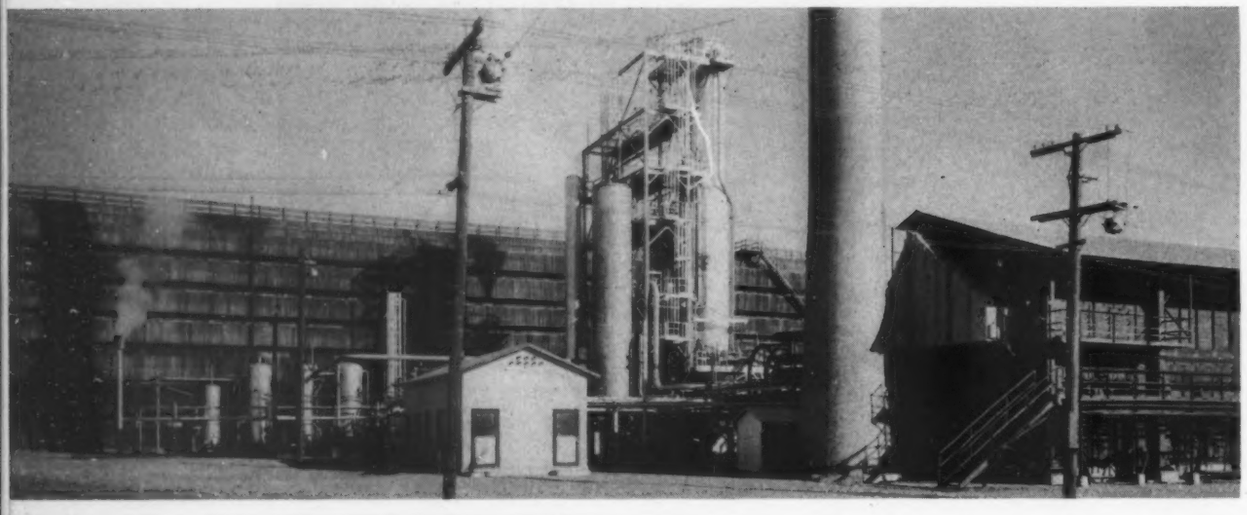


FIGURE 1

General view of General Petroleum Corporation's new cracking installation at Torrance, California.

In the general view, Figure 1, is shown the multi-chamber cracking heater in the right foreground, the fractionating equipment in the center, just beyond the control house, and certain of the various process pumps and accumulator tanks to the left. The plant is operated almost entirely from the instrument panel located in the control house. The temperature of the stream leaving the heater, as well as the temperature in the fractionating towers and pressures at various points in the unit, are controlled automatically.

The multi-chamber heater, shown in Figure 2, is of the suspended wall construction, the walls being made up of light-weight, super-refractory insulating fire brick. It is equipped for burning either gas, commercial fuel oil or pitch made in the unit. The heater is divided into three chambers with one common convection section. Two chambers are devoted to cracking service, while the other is employed for vaporizing the reduced crude charge for production of a small portion of straight-run gas oil. Each of the cracking chambers is in turn divided into a heating section and a soaking section by a curtain wall. With this arrangement it is possible to control the heating curve and thereby obtain optimum cracking conditions. Efficiencies of from 70 to 74 percent are reported without the use of air preheat, due to low air leakage and efficient heat control. Cracking heater charging pumps are of the multi-stage centrifugal type providing pressure differentials of approximately 800 pounds to the square inch.

The interior of the control room is shown in Figure 3. The temperature and flow recording and controlling instruments are sufficient in number and application that the plant may be operated almost entirely from the control room, although auxiliary instrument panels are located at the heater and at the base of the fractionating towers to facilitate operation. The various instruments in the main panel are grouped in such manner as to simplify the operation of any unit of equipment in the plant. Indirect lighting is provided for night operation. One operator is required to observe all the instruments and periodically record all of the various operating conditions on the daily log sheet.

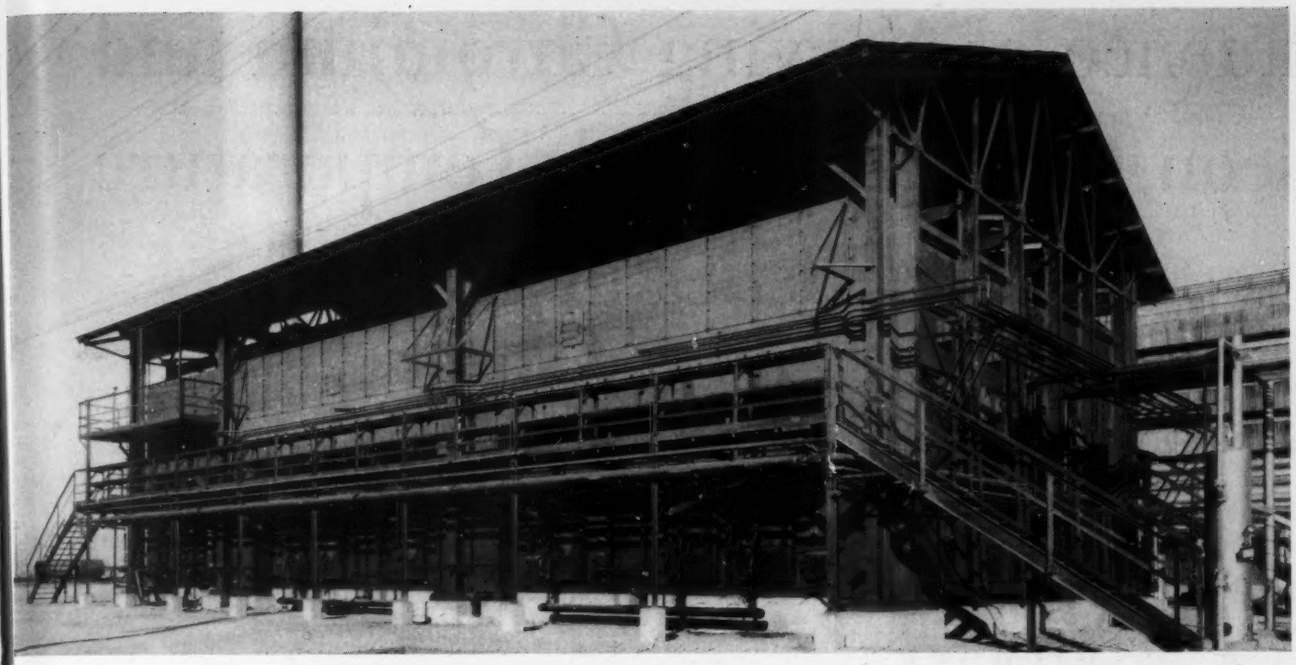
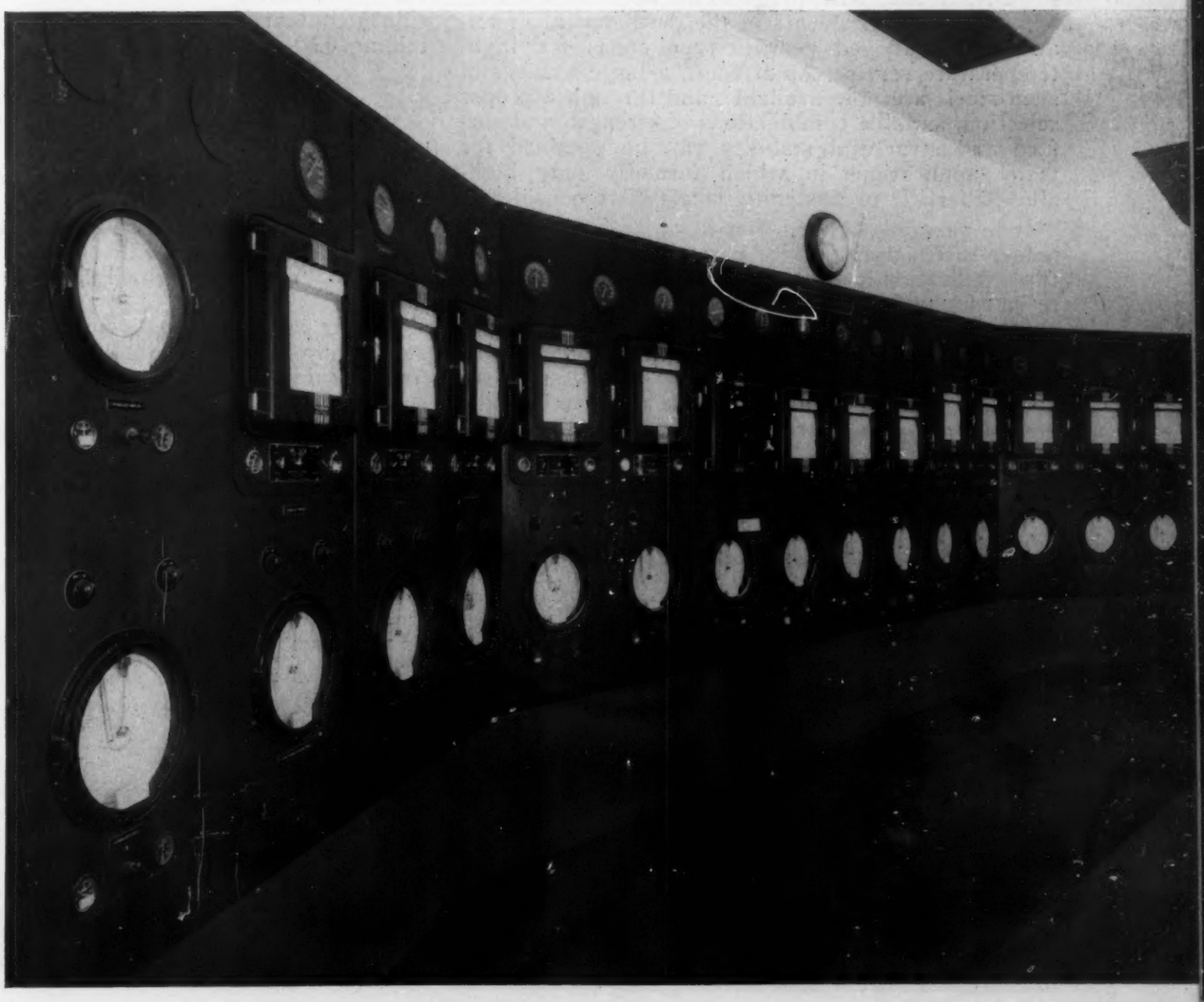


FIGURE 2
Multi-chamber cracking unit heater.

FIGURE 3
Instrument panel in cracking unit control room



Influence of Varying Chromium and Silicon Content on High-Temperature Characteristics of Steels

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CONSIDERABLE progress has been made during the past eight years in the development of relatively low-alloyed pearlitic-type steels for high-temperature service. As a result, a large number of such steels are now available, and through a proper selection, suitable combinations of strength and surface and structural stability can be obtained for many applications in which formerly only high-alloyed ferritic or austenitic steels were considered.

It is generally agreed that in order for a steel to render satisfactory service in a given high-temperature application it must possess sufficient strength to resist, for a suitable length of time, the applied stresses; it must not fracture without deformation or become brittle at room temperature due to the service conditions; and it must possess a sufficient degree of surface stability to resist the attack of the hot gases or liquids with which it is in contact. In addition, it must, of course, possess a suitable combination of room-temperature physical properties which will permit its satisfactory installation.

All the present pearlitic-type steels intended for high-temperature service contain one or more of the following elements: chromium, molybdenum and silicon. It has been generally stated that chromium and molybdenum increase the high-temperature strength, while chromium and silicon improve the surface stability against oxidation and sulphide corrosion. Little information has been available, however, to show the effect of variations in the amounts of these elements on the resulting high-temperature physical properties.

The present paper will discuss the influence on the high temperature properties of variations in the chromium content from 0.0 to 6.0 percent, and in the silicon content from 0.20 to 1.5 percent in steels containing 0.50 percent molybdenum.

STEELS CONSIDERED

The steels considered were obtained from the Timken Steel and Tube Division of The Timken Roller Bearing Company and were taken from commercial basic electric-arc heats. They were all available in the form of hot-rolled 1-inch round bars. Their chemical composition, McQuaid-Ehn grain size, heat-treatment and resulting Brinell hardness are given in Table 1.

Insofar as the silicon content is concerned, the steels may be divided into three groups, with the first containing 1.0 to 1.5 percent of this element, the second 0.50 to 1.0 percent, and the third 0.50 max. percent. In the first and third groups the chromium

TABLE 1
Chemical Composition, Grain Size, Heat Treatment and Brinell Hardness

Steel Designation	Chemical Composition, Percent							McQuaid-Ehn Grain Size	Heat-Treatment, ° F.	Brinell Hardness
	C	Mn	Si	S	P	Cr	Mo			
Steels With 1.0–1.5 Silicon										
Si-Mo	.11	.19	1.35	.012	.010	....	.50	6 to 8	Ann. 1550	146
Si-Cr-Mo 1	.15	.42	1.37	.016	.017	1.30	.54	6 to 8	Ann. 1550	156
Si-Cr-Mo 2	.09	.41	1.32	.017	.010	2.06	.51	4 to 6	Ann. 1550	146
Si-Cr-Mo 3	.12	.43	1.57	.014	.008	3.26	.50	4 to 6	Ann. 1550	159
Si-Cr-Mo 5	.10	.38	1.55	.016	.009	4.83	.51	4 to 6	Ann. 1550	156
Steels With 0.50–1.0 Silicon										
Si-Cr-Mo	.07	.42	.72	.015	.014	1.23	.54	4 to 6	Ann. 1550	123
Si-Cr-Mo 2¼	.11	.41	.78	.013	.012	2.50	.50	6 to 8	Ann. 1550	143
Steels With 0.50 Max. Silicon										
0.50 Mo	.13	.49	.25	.010	.011	....	.52	6 to 8	Ann. 1550	121
1 Cr + Mo	.10	.36	.25	.014	.011	0.97	.55	4 to 6	Ann. 1550	128
2 Cr + Mo	.11	.45	.42	.015	.012	2.08	.50	6 to 8	Ann. 1550	131
4-6 Cr + Mo	.10	.45	.18	.015	.017	5.09	.55	6 to 8	Ann. 1550	128

content ranges from 0.0 to 5.0 percent, and in the second group from 1.25 to 2.50 percent.

All the steels were likewise given the same heat treatment, namely an anneal from 1550° F., and consequently observed differences in their physical characteristics should be mainly due to variations in the chromium and silicon contents.

It is true that a variation exists in the carbon content, the amount of this element present varying from 0.07 to 0.15 percent. While this variation may be sufficient to have some influence on the room-temperature physical properties, it is not believed to be sufficient to appreciably affect the high temperature characteristics.

ROOM TEMPERATURE PHYSICAL PROPERTIES

The room-temperature physical properties of these 11 steels are shown graphically in Figure 1. The chromium content is plotted as the abscissa, and for each of the characteristics three sets of results are included, one corresponding to a silicon content of 0.50 max. percent, another to a content of 0.50 to 1.0 percent, and the third to a content of 1.0 to 1.5 percent. This method of presentation is believed to show definitely the influence of variations in the chromium and silicon content.

Varying Chromium Content

First considering the strength characteristics, that is, the tensile strength, yield stress, and proportional limit values, it will be noted that variations in the chromium content do not produce the same general influence in all cases. With the tensile strength values there is a tendency for the strength to increase as the chromium content is raised to 5.0 percent with the degree of increase being the more pronounced in the 1.0 to 1.5 percent silicon steels and the least marked in the 0.50 max. percent silicon steels. The maximum value of 85,000 pounds resulted from the steel containing 3.25 percent chromium—1.57 percent silicon.

In the case of the yield-stress values, increasing the chromium content to approximately 1.0 percent resulted in an improvement while a further increase produced a decrease in both the lowest- and highest-silicon steels. With the intermediate silicon steels, the point at which the influence of increasing chromium content changes lies at or above 2.5 percent chromium.

Likewise, with the proportional limit values, an increase in the chromium content above 1.0 percent tends to decrease this value. An exception occurs in the 1.0 to 1.5 percent silicon steels in that a second increase occurs as the chromium is raised above 3.25 percent.

Insofar as the ductility is concerned, increasing chromium content tends to increase the reduction-of-area values but has no consistent influence on the elongation. A chromium content of 2.0 to 2.5 percent does tend to yield the maximum elongation value for each group of silicon steels.

Increasing chromium content likewise increases the Charpy impact resistance for the lower and higher silicon steels but decreases it for the 0.50 to 1.0 percent silicon steels. The maximum range in values is from 36 to 82 foot-pounds.

As would be expected, variations in chromium content exert the same influence on the Brinell hardness as on the tensile strength. For each group of steels, the hardness first increases and then decreases as the chromium content is raised. The point of inflection appears to vary with the silicon content, occurring at approximately 2.0 percent chromium for the 0.50 max. silicon steels and at 3.25 percent chromium for the 1.0 to 1.5 percent silicon steels.

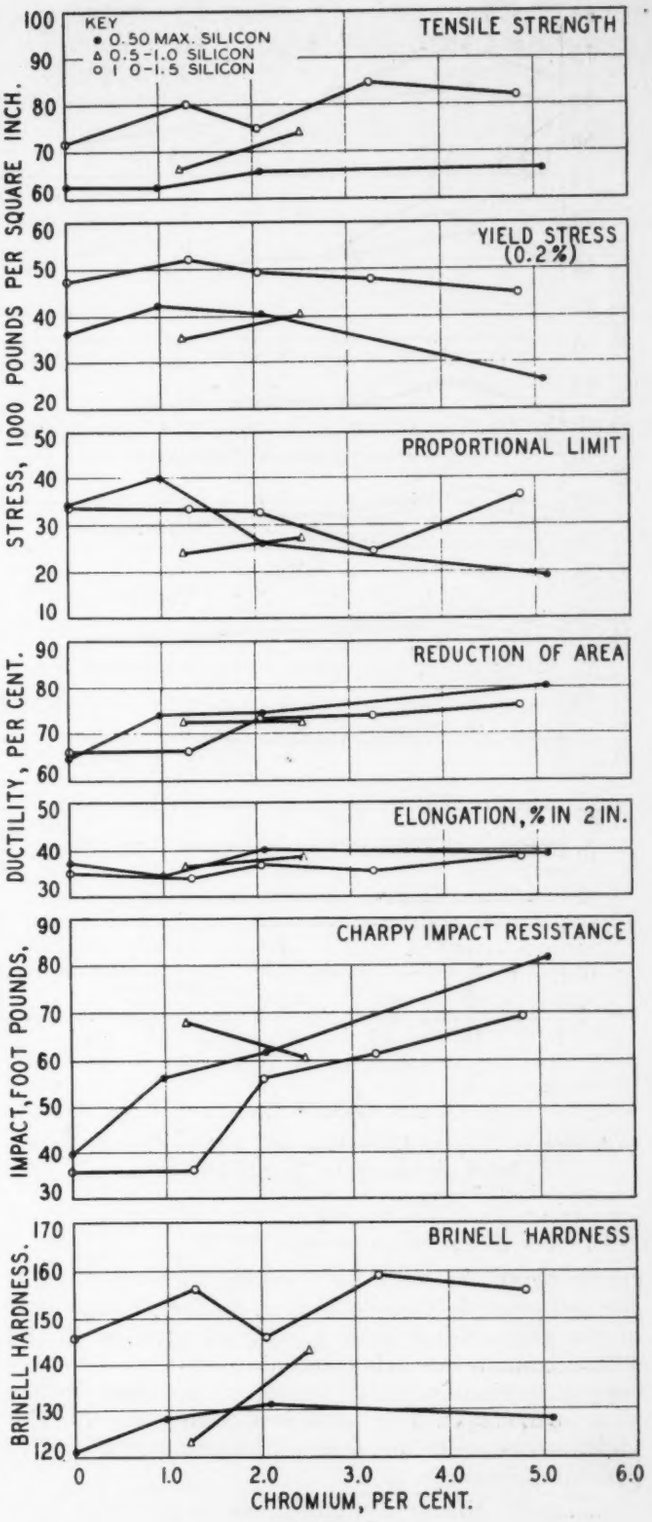


FIGURE 1

Influence of Varying Chromium and Silicon Content on the Room Temperature Physical Characteristics.

Varying Silicon Content

Increasing silicon content tends to increase all of the strength characteristics with the degree of in-

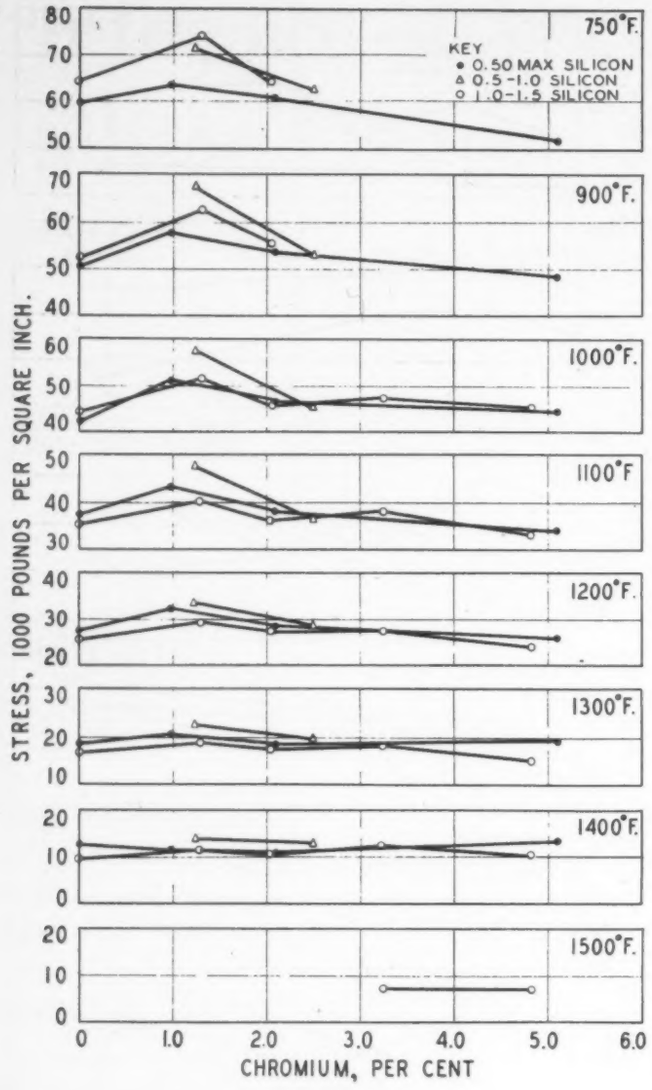


FIGURE 2

Influence of Varying Chromium and Silicon Content on the High Temperature Tensile Strength.

crease being the more pronounced with the tensile-strength and yield-stress values. In fact, in the case of the proportional limit values, an increase in the silicon content in steels containing less than 1.25 percent chromium actually causes a decrease, rather than an increase. The same is likewise true for the yield stress with the steels containing 0.50 to 1.0 percent silicon.

Increased silicon content tends to decrease both the ductility and impact resistance with the degree of decrease being slight in the case of the ductility and somewhat more pronounced with the shock resistance. In no case, however, was the Charpy value below 35 foot-pounds, and in the presence of 2.0 percent or more chromium, the lowest value obtained was 56 foot-pounds.

Silicon increases the Brinell hardness, especially when it is present in an amount of 1.0 to 1.5 percent. The maximum value obtained was, however, slightly below 160 Brinell.

SHORT-TIME HIGH TEMPERATURE TENSILE PROPERTIES

The short-time tensile properties of these steels, at temperatures of 750 to 1500° F. inclusive, are shown in Figures 2 through 6. The same general method of presentation is employed as in Figure 1 except that each figure is devoted to a single characteristic, such as tensile strength, and the subdivisions are based on the test temperature.

Varying Chromium Content

Each of the short-time high-temperature-strength characteristics, Figures 2, 3, and 4, tend to first increase with increasing chromium content and to then decrease as the chromium content is further increased. A chromium content of 1.0 to 1.25 percent imparts the greatest strength for each of the three characteristics at temperatures to 1100° F. inclusive. At 1200 and 1300° F. the same is again true for the tensile strength, but for the remaining two characteristics this maximum occurs at a higher chromium content in the highest silicon steels. At temperatures in excess of 1200° F. changes in the chromium content have little influence on the magnitude of the resulting values.

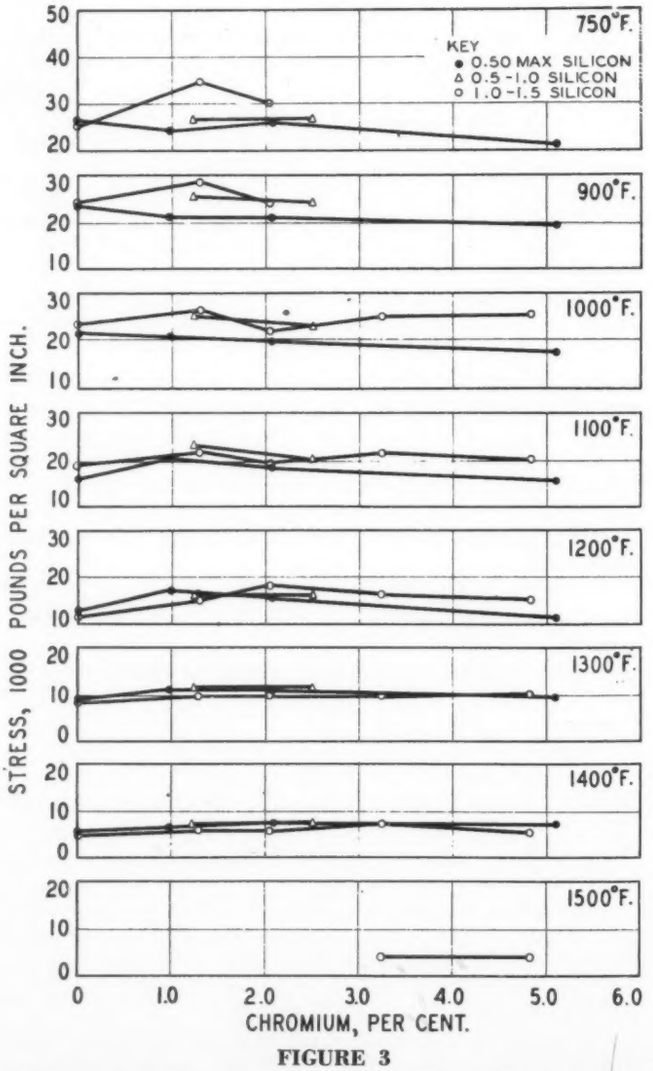


FIGURE 3

Influence of Varying Chromium and Silicon Content on the High Temperature Yield Stress (0.2% Set).

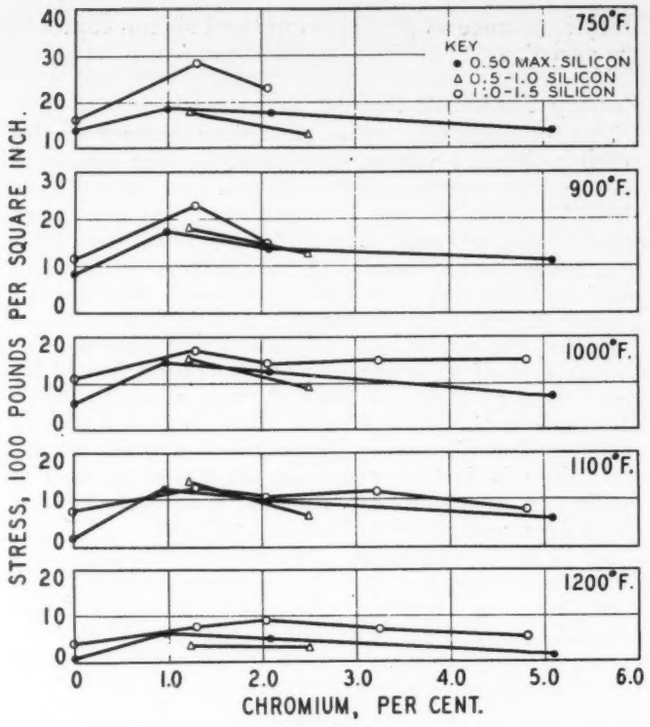


FIGURE 4

Influence of Varying Chromium and Silicon Content on the High Temperature Proportional Limit.

Variations in the chromium content do not produce as uniform an influence on the ductility as on the strength characteristics, Figures 5 and 6. With the two groups of higher silicon steels at temperatures to 1000° F. inclusive, the first increase in chromium content to 1.25 percent decreases the ductility, but further additions increase it. For these same steels at the more elevated temperatures the ductility tends to increase continuously with increasing chromium content, although in the case of the reduction of area values, the maximum increase occurs upon the addition of the first 1.25 percent chromium.

With the 0.50 max. percent silicon steels, the elongation values first increase and then decrease as the chromium content is varied. The change occurs at a chromium content of 1.0 percent at 750, 1300 and 1400° F. and at 2.0 percent for the remaining temperatures. The reduction of area values tend to increase with increasing chromium content at all temperatures except 1000° F. At the latter temperature they decrease continuously from a maximum of 80.0 percent to a minimum of 74 percent.

Varying Silicon Content

At 750 and 900° F. an increase in the silicon content increases each of the three strength characteristics with the maximum improvement occurring with a chromium content of 1.25 percent. At the more elevated temperatures the 1.0 to 1.5 percent silicon steels, as well as the 0.50 to 1.0 percent silicon steel containing 2.5 percent chromium, are either inferior, or equal, to the 0.50 max. percent silicon steels. The proportional limit is, however, in general an exception, for at each of the temperatures considered, the higher-silicon steels tend to possess the greater values.

Insofar as the ductility is concerned, an increase in the silicon content tends to increase the reduction of area and especially the elongation. The differences are more pronounced at the higher chromium contents, and in fact the steel containing 0.50 to 1.0 percent silicon and 1.25 percent chromium possesses in

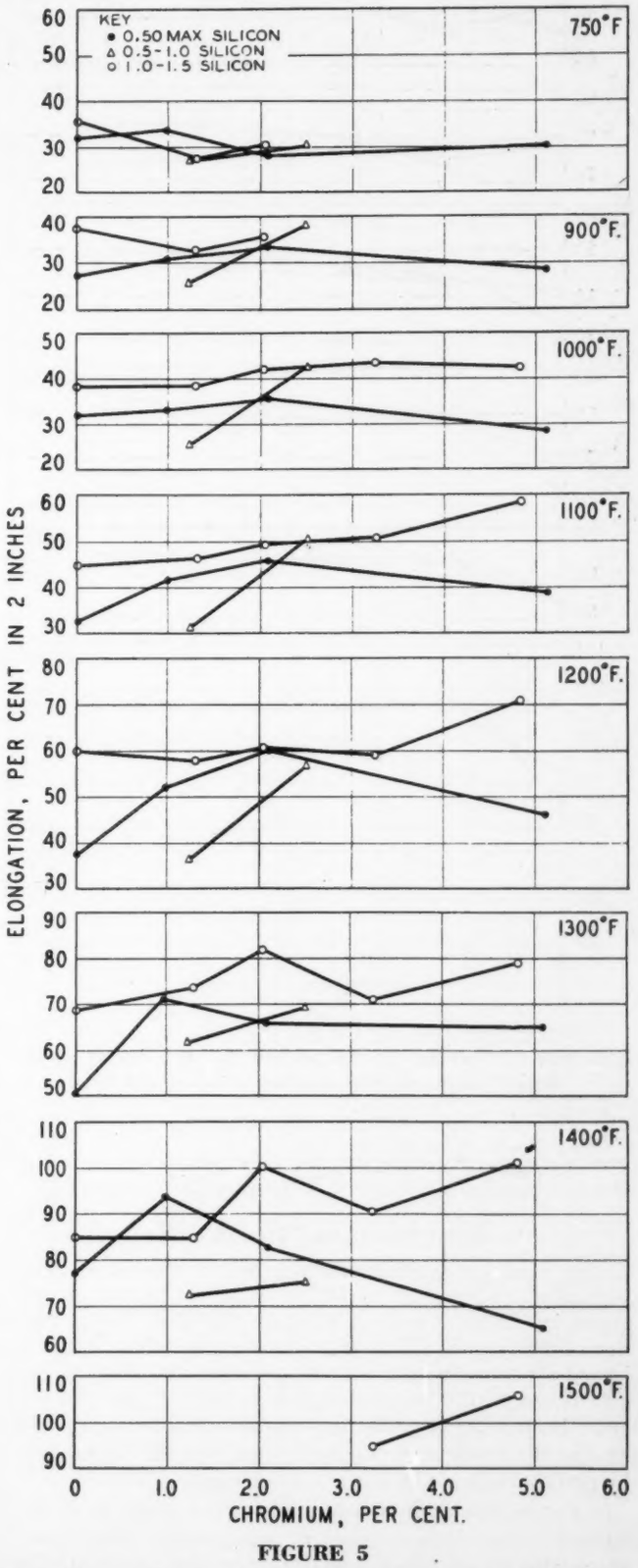


FIGURE 5

Influence of Varying Chromium and Silicon Content on the High Temperature Elongation Values.

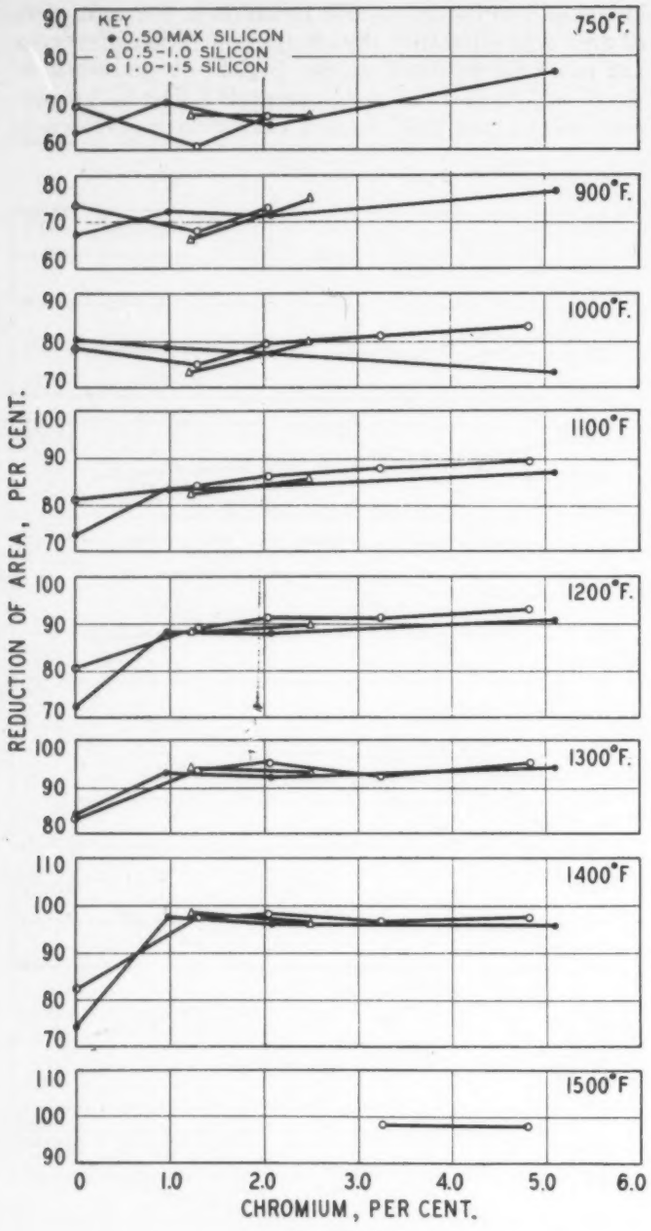


FIGURE 6

Influence of Varying Chromium and Silicon Content on the High Temperature Reduction of Area Values.

practically every case ductility values below those of the corresponding 0.50 max. percent silicon steel.

CREEP CHARACTERISTICS

The creep characteristics of these steels, at temperatures ranging from 800 to 1300° F. inclusive, are given in Table 2 and in Figures 7 and 8. These two figures differ in that the stresses of the first are based on a creep rate of 0.01 percent per 1000 hours, and those of the second on a rate of 0.10 percent per 1000 hours. Again the chromium content is plotted as the abscissa and the individual steels considered in groups based on their silicon content.

As complete comparisons cannot be made as in the case of the characteristics previously considered, since the creep characteristics are not available for each steel at each of the temperatures. Sufficient results are included, however, to show the trend in the creep resistance as the chromium and silicon contents are varied.

Varying Chromium Content

The influence of varying chromium content on the creep resistance varies, depending on the temperature and the creep rate considered. For example, at 800° F., chromium has little influence on the stress required for a creep rate of 0.01 percent per 1000 hours, but an increase in the chromium content beyond 1.25 percent does lower the stress required for a creep rate of 0.10 percent per 1000 hours.

Basing the comparisons on the stress required for a creep rate of 0.10 percent per 1000 hours, it will be noted that at 900 and 1000° F., the creep strength increases as the chromium is raised from 0.0 to 1.25 percent, then decreases, but again increases as the chromium is further raised above 2.0 percent. The maximum strength is, however, obtained with a chromium content of 1.00 to 1.25 percent.

At 1100° F. the creep strength increases as the chromium content is raised to a certain amount and then decreases slightly as the chromium is further increased. With the low-sicilon steels the change occurs at a chromium content of 2.0 percent, and with the high-silicon steels at 3.25 percent chromium.

At 1200° F. the creep strength is changed only slightly as the chromium content is raised to 1.25 percent, increases sharply as the chromium is further increased to 2.0 percent, and decreases slightly as the chromium content is extended beyond 2.0 percent.

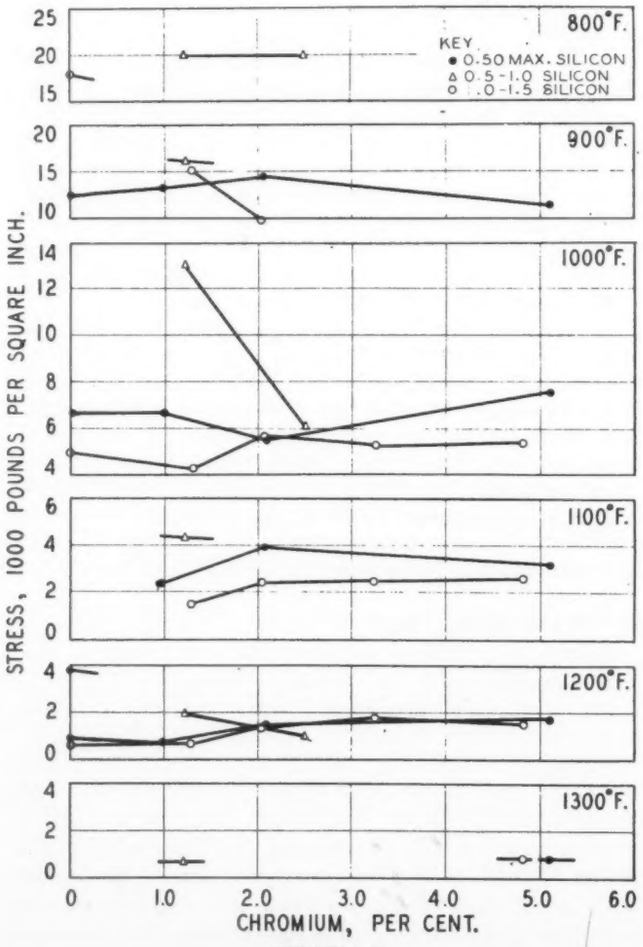


FIGURE 7

Influence of Varying Chromium and Silicon Content on the Creep Strength (0.01%/1000 Hr.).

TABLE 2

Creep Characteristics of Silicon Chromium-Molybdenum Steels with Varying Chromium and Silicon Content

Steel Designation	Stress for Designated Creep Rate at Indicated Temperatures—Rate = Percent per 1,000 Hours											
	800° F.		900° F.		1,000° F.		1,100° F.		1,200° F.		1,300° F.	
	0.01	0.10	0.01	0.10	0.01	0.10	0.01	0.10	0.01	0.10	0.01	0.10
Steels With 1.0 to 1.5 Silicon												
Si-Mo	18,000	29,500	.....	.....	5,000	9,200	.....	.....	720	1,850	.....	.....
Si-Cr-Mo 1	.....	.....	15,100	21,750	4,300	9,200	1,525	3,800	720	1,800	.....	.....
Si-Cr-Mo 2	.....	.....	9,900	13,800	5,700	7,800	2,400	4,600	1,400	3,700	.....	.....
Si-Cr-Mo 3	.....	.....	.....	.....	5,400	8,700	2,500	5,100	1,800	3,550	.....	.....
Si-Cr-Mo 5	.....	.....	.....	.....	5,450	8,700	2,600	4,800	1,600	2,900	920	1,450
Steels With 0.50 to 1.0 Silicon												
Si-Cr-Mo	20,000	29,000	16,000	25,000	13,000	22,000	4,300	6,800	1,950	3,950	700	800
Si-Cr-Mo 2½	20,000	25,000	.....	.....	6,100	9,300	.....	.....	1,000	2,325	.....	.....
Steels With 0.50 Max. Silicon												
0.50 Mo	.....	.....	12,500	18,800	6,700	10,800	1,800	4,000	900	2,200	.....	.....
1 Cr + Mo	.....	.....	.....	20,500	.....	12,000	.....	4,600	.....	1,625	.....	.....
2 Cr + Mo	.....	.....	14,500	19,300	5,600	8,900	4,000	6,000	1,500	3,500	.....	.....
4-6 Cr + Mo	.....	.....	11,500	15,250	7,600	10,100	3,200	5,850	1,700	2,800	890	1,950

The same tendencies are in general observed at temperatures of 900° F. and higher when the comparisons are based on the stress required for a creep rate of 0.01 percent per 1000 hours. Certain of the changes are, however, somewhat more pronounced and in certain cases differences exist in the amount of chromium required to impart the maximum creep resistance.

Varying Silicon Content

Results are not available from a sufficient number of steels at 800° F. to definitely indicate the influence of variations in the silicon content on the resulting creep resistance. At 900° F., however, the results show that with a chromium content of 1.0 to 1.25 percent the creep resistance is not lowered as the silicon is raised to 1.5 percent; with a chromium content of 2.5 percent, however, it is.

At 1000 and 1100° F. the creep resistance is lowered through the addition of 1.0 to 1.5 percent silicon. Again, however, with the lower chromium content the addition of 0.50 to 1.0 percent silicon increases the creep strength to a considerable extent, and with the 2.5 percent chromium type of steel, this same amount of silicon has no appreciable influence.

At 1200 and 1300° F. the addition of 1.0 to 1.5 percent silicon does not have a pronounced influence on the resulting creep strength, while the addition of 0.50 to 1.0 percent silicon increases the creep resistance of the lower-chromium steels and decreases the resistance of the 2.5 percent chromium steels.

Since silicon is added primarily to increase the surface stability, rather than the strength, it is not surprising that a decrease in the creep strength occurs at temperatures such as 1000 and 1100° F. It should be realized that in the creep tests, which were conducted for 1000 hours, the degree of surface stability is not a deciding factor in determining the results obtained. Over more prolonged testing-time periods, or in actual operation, it is evident that without a high degree of surface stability the cross-section of the metal would be reduced, the unit stress increased, and the life of the part thus shortened. In other words, creep strength by itself may not be a true criterion of a metal's suitability for high-temperature service.

RUPTURE STRENGTH

The rupture strength of certain of these steels at temperatures of 900 to 1500° F. inclusive, are given in Table 3 and in Figure 9. The stresses given are those required for rupture in 100,000 hours. It is true that these stresses are based on extrapolation, since

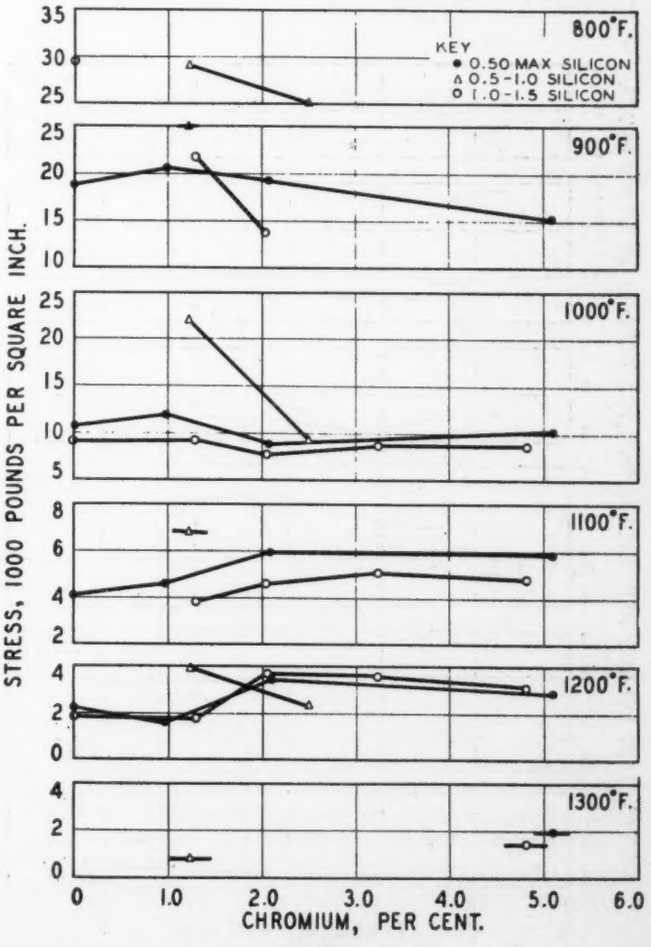


FIGURE 8

Influence of Varying Chromium and Silicon Content on the Creep Strength (0.01%/1000 Hrs.).

TABLE 3

Stress-Rupture Characteristics of Silicon-Chromium-Molybdenum Steels with Varying Chromium and Silicon Content

Steel Designation	Stress for Rupture in 100,000 Hours at Indicated Temperatures						
	900° F.	1,000° F.	1,100° F.	1,200° F.	1,300° F.	1,400° F.	1,500° F.
Steels With 1.0 to 1.5 Silicon							
Si-Cr-Mo 1	.....	20,250	5,250	2,650	.....	.....	.....
Si-Cr-Mo 2	23,000	11,750	4,400	2,800	.....	.....	.....
Si-Cr-Mo 3	.....	11,250	5,000	3,400	1,950	.....	270
Si-Cr-Mo 5	.....	10,000	5,400	3,150	1,850	.....	470
Steels With 0.50 to 1.0 Silicon							
Si-Cr-Mo	.....	9,000	.....	2,200	700	150	.....
Steels With 0.50 Max. Silicon							
1 Cr + Mo	.....	27,500	4,500	1,700	.....	.....	.....
4-6 Cr + Mo	.....	14,500	6,700	3,000	1,300	.....	105

the average actual testing time was of the order of 2000 to 3000 hours. However, because of the straight line logarithmic relationship which results from tests of this type and the fact that the values considered are fixed and not dependent on time, this degree of extrapolation is not believed to be excessive.

Varying Chromium Content

The influence of variations in the chromium content on the rupture strength varies depending on the temperature considered. At 900° F. sufficient results are not available to permit comparisons. At 1000° F., however, the tendency is for the rupture strength to decrease as the chromium content is increased with the sharpest drop occurring as the chromium is raised to 2.0 percent. The decrease beyond 2.0 percent is, however, slight.

At 1100° F. the rupture strength first decreases and then increases as chromium is added in amounts beyond 2.0 percent. On the other hand, at 1200 and 1300° F. a chromium content of 3.25 percent appears to impart the greatest degree of load-carrying ability. At 1500° F., however, the maximum chromium content produced the greatest rupture strength.

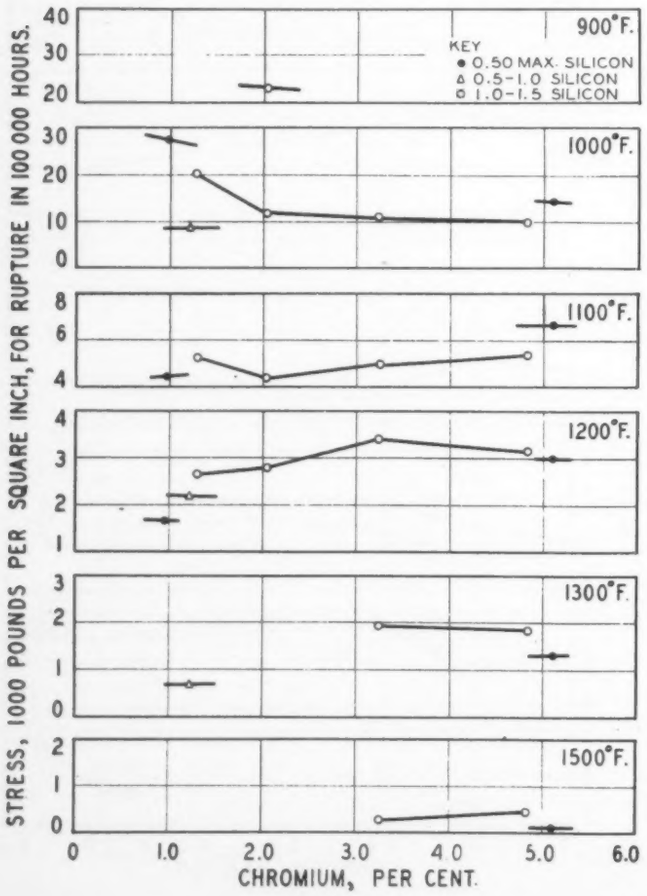


FIGURE 9

Influence of Varying Chromium and Silicon Content on the Rupture Strength (100,000 Hours).

Varying Silicon Content

As in the case of the chromium content, the influence of variations in the silicon content on the rupture strength varies depending on the temperature. At 1000° F. an increase in the silicon content lowered the rupture strength for all the chromium contents considered. The same is likewise true at 1100° F. for the higher chromium contents but not the lower ones.

At the more elevated temperatures, however, the load-carrying ability is decidedly improved by the addition of 1.0 to 1.5 percent silicon. As will be discussed later, this improvement results from the greater surface stability of these higher-silicon steels.

In all these tests slightly oxidizing conditions were present. If the atmosphere had been more highly oxidizing the higher-silicon steels would have showed to even greater advantage at the higher temperature and would have been superior, rather than inferior, to the lower-silicon steels at the lower temperatures.

CREEP STRENGTH VERSUS RUPTURE STRENGTH

Since the creep characteristics are widely used as a basis for the design of high-temperature equipment, a comparison of the results from the standard creep and the rupture tests should be of interest. Such a comparison is given in Table 4, with the steels again being grouped according to their silicon content.

For 4 of the 6 steels the ratio of the creep strength (0.01 percent) to the rupture strength (100,000 hours) is of the order of 0.50. For these steels therefore the 100,000 hour rupture strength, divided by two, yields a stress value nearly identical to that determined from the creep test for a creep rate of 0.01 percent per 1000 hours. The rupture test is, how-

ever, the more simple of the two tests and also yields additional information with respect to the high-temperature-ductility characteristics.

Variations in the silicon content have little, if any, influence on this ratio. For example, the standard 4-6 Cr + Mo steel, containing 0.18 percent silicon, and Si-Cr-Mo 5, containing 1.55 percent of this element, possess approximately the same ratio at each of the temperatures considered, with the possible exception of 1300° F. At this latter temperature the ratio of the 4-6 Cr + Mo steel is influenced by the severe oxidation which occurs.

The magnitude of the ratio does, however, appear to depend on the chromium content. All of the steels possessing a ratio decidedly above or below 0.50 contain less than 2.0 percent chromium.

SURFACE STABILITY

As stated previously, a steel can render satisfactory service at elevated temperatures only if it possesses sufficient surface stability to resist, to the required degree, the attack of the medium with which it is to be in contact. In many high-temperature tubular applications the outside of the tube is subjected to oxidation and the inside to corrosion, which, in the case of cracking tubes, may be largely of the sulphide type.

Corrosion Resistance

Laboratory corrosion tests were not undertaken because of the uncertainties as to whether or not laboratory tests of this type can prophesy service performance. It is generally agreed, however, that the resistance to sulphide corrosion is dependent on the chromium content, with the greater degree of improvement occurring as the chromium is first increased to 2.0 percent. Further improvement results as the chromium is increased beyond 2.0 percent, but at a decreasing rate.

Information with respect to the influence of silicon content on the resistance to sulphide corrosion is not as definitely established as in the case of chromium. However, results now becoming available do definitely indicate that greater corrosion resistance is obtained through the use of higher silicon contents.

Oxidation Resistance

The comparative oxidation resistance of these steels at temperatures of 1250 to 1750° F. is shown in

TABLE 4

Relationship of Creep Strength to Rupture Strength

Steel Designation	Ratio of Creep Strength (0.01%) to Rupture Strength—(100,000 Hours)				
	900° F.	1000° F.	1100° F.	1200° F.	1300° F.
Steels With 1.0 to 1.5 Silicon					
Si-Cr-Mo 1	....	0.22	0.29	0.28	....
Si-Cr-Mo 2	0.43	0.49	0.55	0.50	....
Si-Cr-Mo 3	....	0.48	0.50	0.53	....
Si-Cr-Mo 5	....	0.55	0.48	0.51	0.50
Steels With 0.50 to 1.0 Silicon					
Si-Cr-Mo	....	1.44	....	0.89	....
Steels With 0.50 Max. Silicon					
4-6Cr + Mo	....	0.52	0.48	0.57	0.69

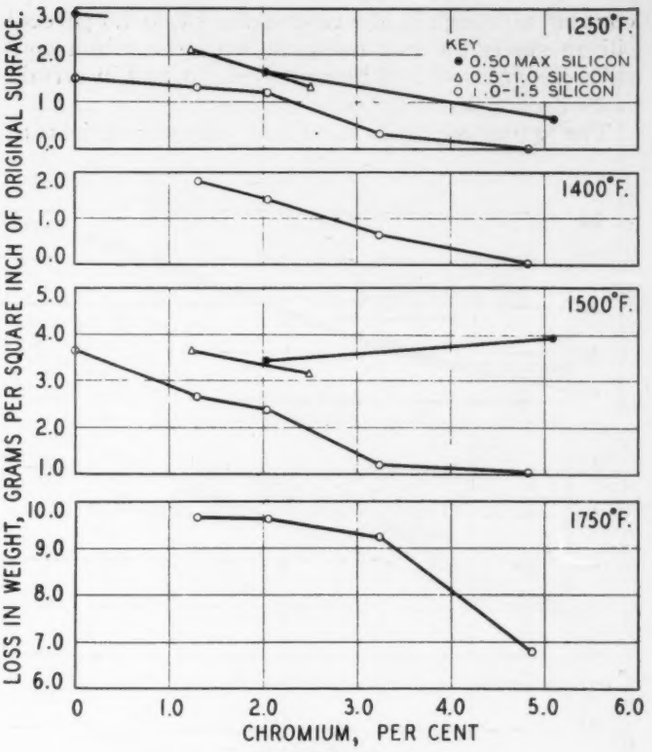


FIGURE 10

Influence of Varying Chromium and Silicon Content on the Oxidation Resistance.

Figure 10. The specimens were heated continuously in air for 1000 hours, the scale removed by an electrolytic method, and the results given as weight loss in grams per square inch of original surface.

The influence of chromium additions on the oxidation resistance varies, depending on the silicon content. With the steels containing 1.0 to 1.5 percent silicon, an increase in the chromium content improves the resistance at each of the temperatures with the greatest degree of improvement resulting when the chromium exceeds 2.0 percent. Increasing chromium content likewise improves the oxidation resistance of the 0.50 to 1.0 percent silicon steels, but with the 0.50 max. percent silicon steels this is true only at 1250° F. At the higher temperatures it has little influence on the resistance of the lower-silicon steels.

Increased silicon content greatly improves the oxidation resistance. In fact, on the basis of these, as well as other results, it appears that, in the presence of chromium, silicon is seven times as effective as chromium in imparting resistance to oxidation. The magnitude of its influence is well demonstrated by the comparative behavior of the 4-6 Cr + Mo and Si-Cr-Mo 5 steels at 1500° F.

HOT IMPACT RESISTANCE

The impact resistance of these steels, at temperatures varying from 750 to 1500° F., is shown graphically in Figure 11. One set of specimens of each steel was held at temperature one hour prior to breaking while another set was held for 1000 hours. Again the chromium content is plotted as the abscissa and the steels arranged in groups according to their silicon content.

Varying Chromium Content

At temperatures of 750, 900 and 1000° F. the impact resistance increases with increasing chromium

content, although in the case of the 1.0 to 1.5 percent silicon steels the improvement with chromium contents in excess of 3.25 percent is slight and in certain cases even a small decrease occurs.

The same general condition likeness exists at 1100° F. for chromium contents in excess of 1.0 percent and at 1200° F. for chromium contents in excess of 2.0 percent. At the higher temperatures an increase in the chromium content from 3.25 to 5.0 percent has only a slight influence.

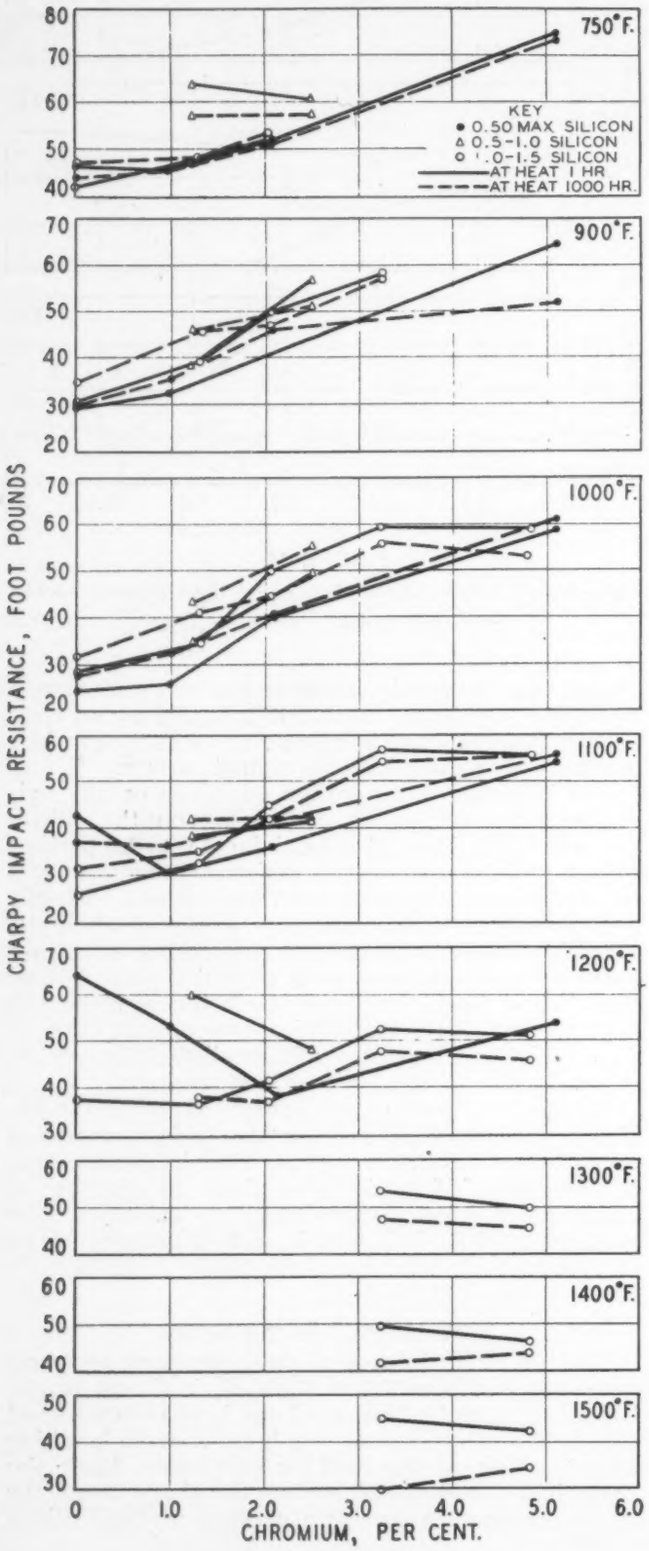


FIGURE 11

Influence of Varying Chromium and Silicon Content on the Hot Impact Resistance.

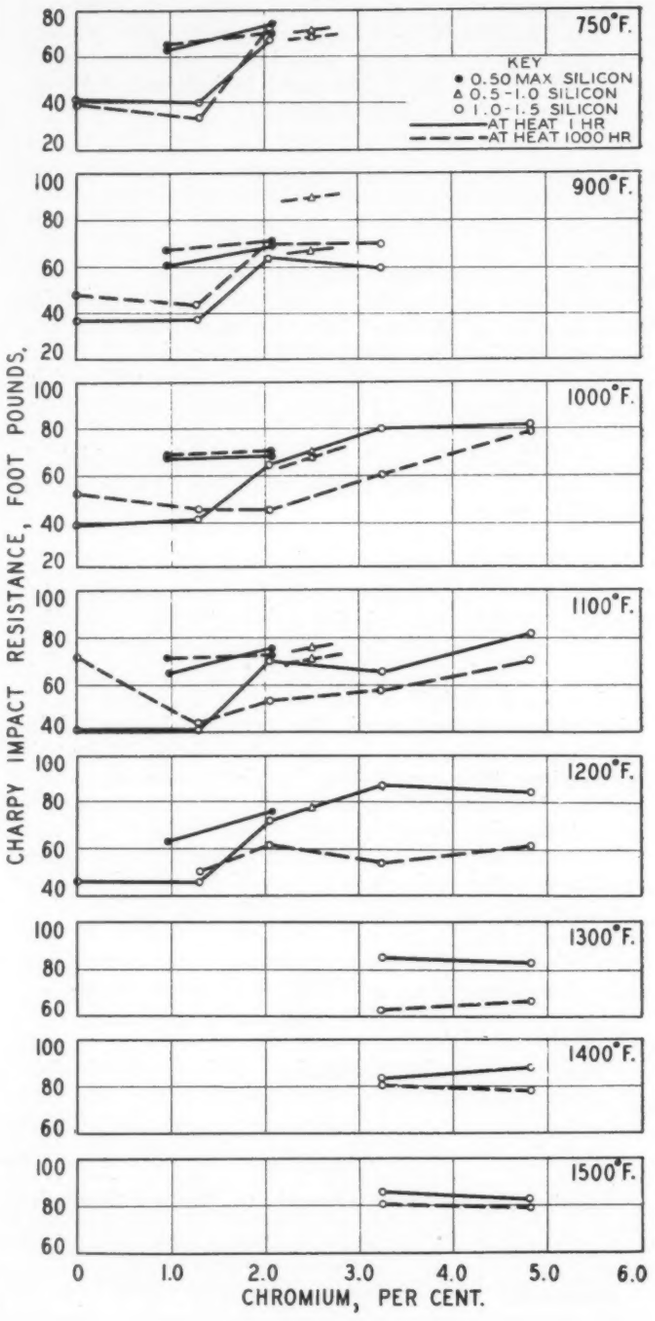
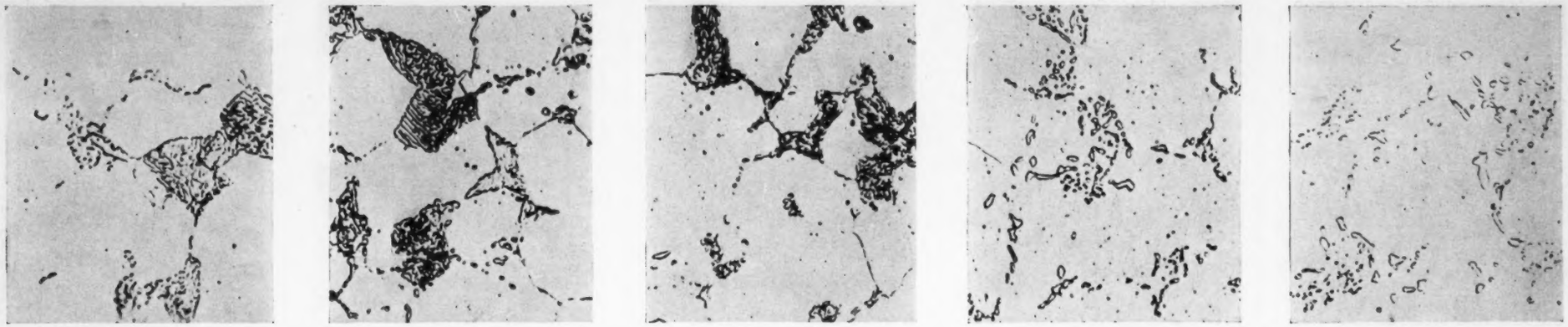


FIGURE 12

Influence of Varying Chromium and Silicon Content on the Room Temperature Impact Resistance after Air Cooling from Designated Temperatures.

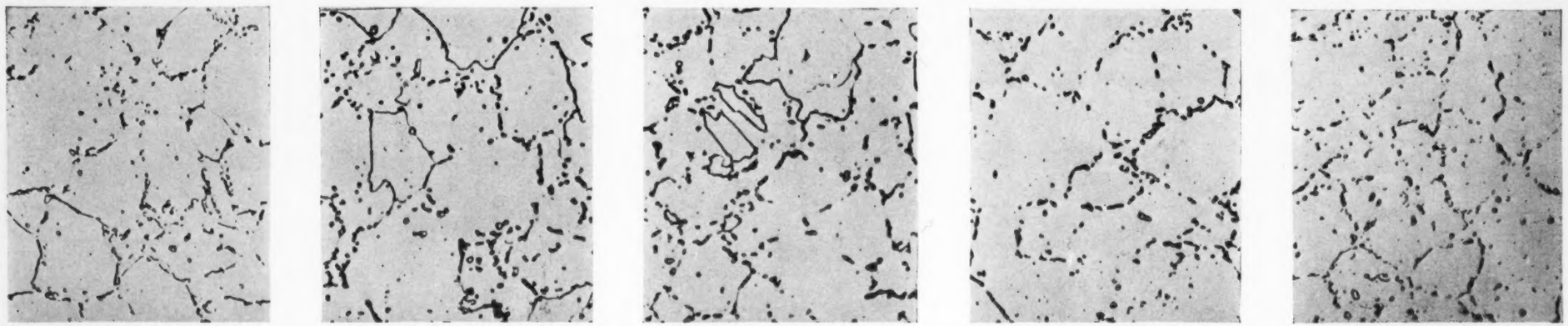
Varying Silicon Content

An increase in the silicon content to 1.0 to 1.5 percent has little influence on the impact resistance at 750° F. but at temperatures of 900 to 1100° F. it tends to increase the resistance to shock. In general the maximum resistance is possessed by the steel containing 3.25 percent chromium—1.57 percent sil-



Original Structure | 900° F.—1,300 Hours 15,000 Pounds | 1,000° F.—1,100 Hours 10,000 Pounds | 1,100° F.—1,000 Hours 3,000 Pounds | 1,200° F.—1,160 Hours 3,000 Pounds

(a) Carbon-Molybdenum Steel



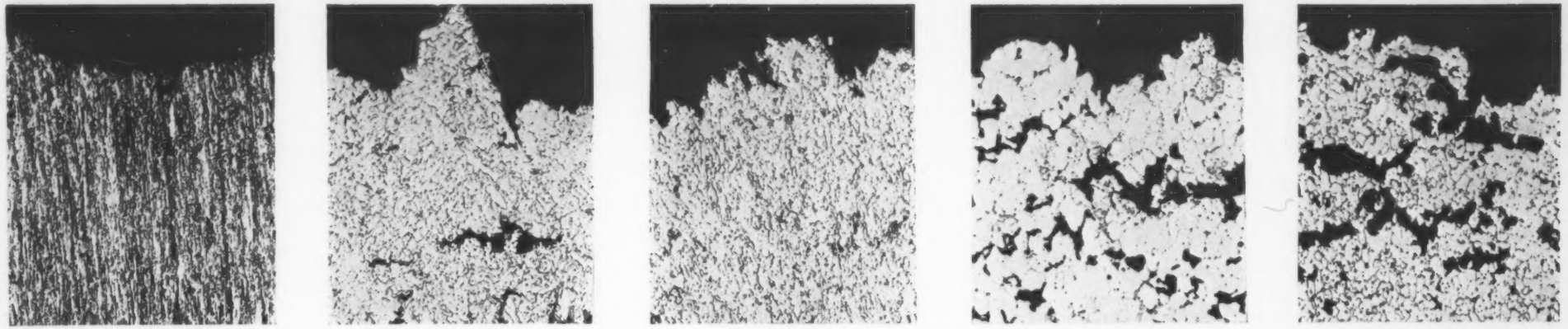
Original Structure | 900° F.—1,065 Hours 12,500 Pounds | 1,000° F.—1,020 Hours 7,000 Pounds | 1,100° F.—1,040 Hours 4,000 Pounds | 1,200° F.—1,000 Hours 3,000 Pounds

(b) Si-Cr-Mo 2 Steel

FIGURE 13

Influence of Time, Temperature and Stress (Creep Tests) on the Microstructures of Two Types of Steels — X1000D.

February, 1939—A Gulf Publishing Company Publication



1,000° F.—1,600 Hours
20,000 Pounds

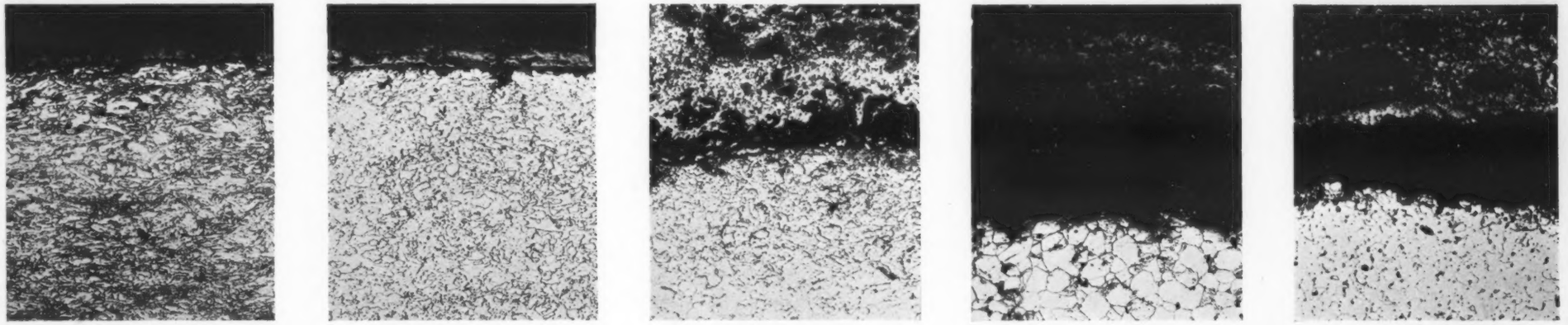
1,100° F.—1,452 Hours
11,000 Pounds

1,200° F.—2,170 Hours
6,000 Pounds

1,300° F.—5,394 Hours
2,400 Pounds

1,500° F.—890 Hours
700 Pounds

(a) Microstructures of the Actual Fractures showing the Type and Characteristics of the Fracture.



1,000° F.—1,600 Hours
20,000 Pounds

1,100° F.—1,452 Hours
11,000 Pounds

1,200° F.—2,710 Hours
6,000 Pounds

1,300° F.—5,394 Hours
2,400 Pounds

1,500° F.—890 Hours
700 Pounds

(b) Microstructures of the Surface, showing the Degree of Surface and Structural Stability.

FIGURE 14

Influence of Time, Temperature and Stress (Rupture Tests) on the Surface and Structural Stability of 4-6 Cr.+Mo. Steel—X100D.

TABLE 5

Influence of Conditions of Creep Tests on the Room-Temperature Tensile Properties of the Completed Creep Specimens

STEEL DESIGNATION	Designated Properties Before and After Creep Tests at Indicated Temperatures							
	Tensile Strength, Pounds per Square Inch				Elongation, Percent in Two Inches			
	Original	1,000° F.	1,100° F.	1,200° F.	Original	1,000° F.	1,100° F.	1,200° F.
Steels With 1.0 to 1.5 Silicon								
Si-Mo	71,750	70,900	.....	69,100	35.3	36.5	....	34.0
Si-Cr-Mo 1	80,400	81,250	81,000	76,000	34.0	34.5	34.0	32.5
Si-Cr-Mo 2	75,100	75,100	74,750	72,400	37.0	38.0	36.0	33.8
Si-Cr-Mo 3	84,900	83,400	83,500	81,100	35.8	33.3	35.5	36.0
Si-Cr-Mo 5	82,100	81,500	79,900	80,400	38.8	37.5	37.5	38.3
Steels With 0.50 to 1.0 Silicon								
Si-Cr-Mo	66,500	67,500	68,500	60,700	36.5	35.8	34.5	34.5
Si-Cr-Mo 2½	74,400	73,400	.....	70,000	38.5	38.8	....	35.3
Steels With 0.50 Max. Silicon								
0.50 Mo	62,100	61,100	60,900	55,900	37.5	40.3	37.8	31.5
1 Cr + Mo	62,500	63,000	62,750	56,650	34.5	41.0	41.5	36.3
2 Cr + Mo	65,900	65,100	65,700	63,800	40.3	42.0	42.0	37.5
4-6 Cr + Mo	66,600	67,000	77,300	64,400	39.0	38.8	37.0	36.3

Note: Creep tests conducted for a minimum of 1,000 hours and each reported value is the average of tests on two completed creep specimens.

icon. At 1200° F. the addition of this amount of silicon lowers the impact resistance of the lower- and higher-chromium steels but increases that of the intermediate-chromium steels.

At each of the temperatures the addition of 0.50 to 1.0 percent silicon improved the impact resistance as compared to that of the low-silicon steels. The degree of improvement was most pronounced at 750 and 1200° F.

All of the steels considered did, however, possess an ample degree of hot impact resistance at each of the temperatures considered. The minimum values were obtained at 1000° F. but, on the basis of the 1-hour test, this value was 24 foot-pounds and holding at temperature for 1000 hours increased this resistance to 28 foot-punds. The steel possessing this minimum value was the standard 0.50 percent molybdenum analysis.

DEGREE OF HIGH-TEMPERATURE STABILITY

The stability of these steels under the combined influence of time, temperature and stress was determined by tensile and impact tests on the completed creep specimens, by the hot ductility of the more prolonged stress-rupture specimens, and by a metallographic examination of both the creep and stress-rupture specimens. Impact tests on specimens air cooled from a series of temperatures were used to determine the effect of time and temperature in the absence of stress.

Heat Embrittlement Tests

The results obtained from room temperature Charpy impact tests on specimens which had been held at a series of temperatures, ranging from 750 to 1500° F., for both 1 hour and 1000 hours, followed by air cooling, are given in Figure 12. These results are of value in indicating the influence of time and temperature, in the absence of stress, on the impact resistance and thus on the structural stability. The findings indicate the susceptibility of a steel to temper embrittlement.

The addition of chromium tends to increase the room-temperature-impact resistance after air cooling, although in many cases the resistance is either unchanged or decreased as the chromium is first increased to 1.25 percent and likewise changed little as the chromium is increased beyond 3.25 percent. In every case, however, an appreciable improvement was obtained as the chromium was increased from about 1.0 percent to 2 percent.

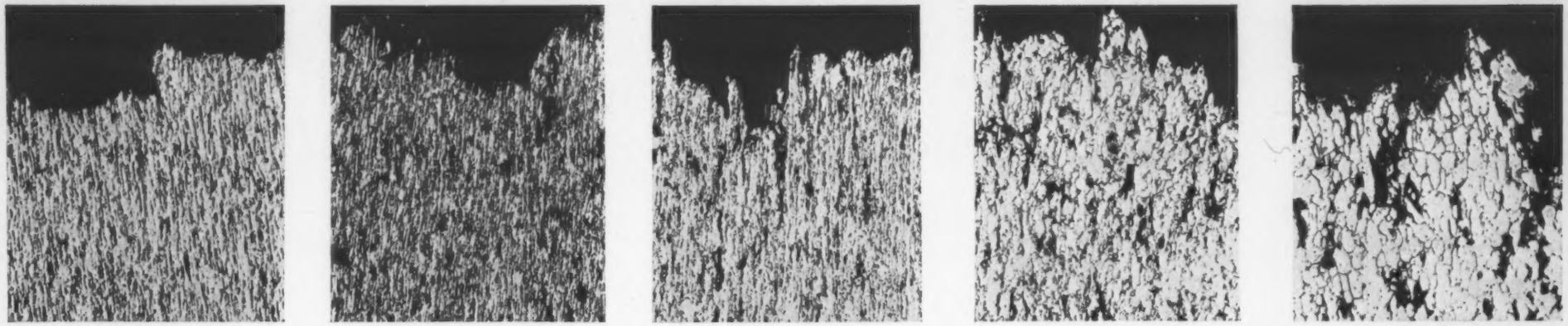
An increased silicon content tends to lower the impact resistance when the chromium content is 1.25 percent or less. For the higher-chromium steels, increased silicon content has little influence on the basis of the 1-hour heating tests. At temperatures of 1000 and 1100° F., and for a heating time of 1000 hours, an increase in the silicon content beyond 1.0 percent did result in a lowered shock resistance. The minimum Charpy value obtained was, however, of the order of 40 foot-pounds, which would be ample for commercial applications.

Tensile Properties of Completed Creep Specimens

The room-temperature tensile properties of the completed creep specimens are given in Table 5. The comparisons are limited to temperatures of 1000, 1100 and 1200° F. and are based only on the tensile strength and elongation values, since these two characteristics give, in general, a good indication of the influence of the creep tests on the resulting room-temperature properties.

Insofar as the tensile strength is concerned, the creep tests at 1000 and 1100° F. had no appreciable influence on the resulting room-temperature properties, regardless of the chromium or silicon content. The creep tests at 1200° F. did, however lower the room-temperature tensile strength with the degree of decrease being the more pronounced for the lower-chromium and lower-silicon steels. For example, in the case of the Si-Mo steel the decrease was of the order of 2500 pounds per square inch, and with the 0.50-Mo steel, about 6000 pounds. This observed decrease, after the creep tests at 1200° F., is largely due to spheroidization, and since the higher-alloyed steels are spheroidized, in the original condition, they would not be expected to show as pronounced a change in their room-temperature tensile strength.

The creep tests exerted the same general influence on the resulting room-temperature elongation values as on the tensile strength, but the changes were less



1,000° F.—930 Hours
17,500 Pounds

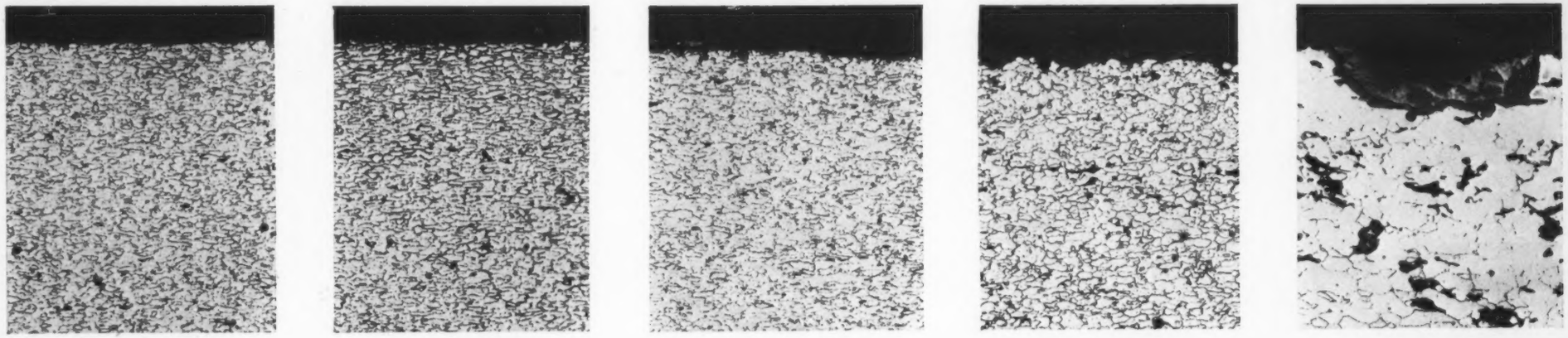
1,100° F.—1,044 Hours
10,000 Pounds

1,200° F.—927 Hours
6,000 Pounds

1,300° F.—2,987 Hours
3,200 Pounds

1,500° F.—2,268 Hours
1,000 Pounds

(a) Microstructures of the Actual Fractures, showing the Type and Characteristics of the Fracture.



1,000° F.—930 Hours
17,500 Pounds

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10,000 Pounds

1,200° F.—927 Hours
6,000 Pounds

1,300° F.—2,987 Hours
3,200 Pounds

1,500° F.—2,268 Hours
1,000 Pounds

(b) Microstructures of the Surface, showing the Dregree of Surface and Structural Stability.

FIGURE 15

Influence of Time, Temperature and Stress (Rupture Tests) on the Surface and Structural Stability of Si-Cr-Mo 5 Steel—X100D.

TABLE 6

Influence of Conditions of Creep Tests on the Room-Temperature Impact Resistance of the Completed Creep Specimens

STEEL DESIGNATION	Izod Impact Resistance*, Ft.-Lb., After Creep Tests at Indicated Temperatures					
	Original	800° F.	900° F.	1,000° F.	1,100° F.	1,200° F.
Steels With 1.0 to 1.5 Silicon						
Si-Mo	54.5	47.5	....	47.5	....	90.0
Si-Cr-Mo 1	59.0	....	47.3	50.8	51.0	57.0
Si-Cr-Mo 2	87.0	....	90.5	81.5	68.8	83.5
Si-Cr-Mo 3	80.0	....	....	108.0	67.5	60.0
Si-Cr-Mo 5	100.0	....	....	101.5	68.0	80.8
Steels With 0.50 to 1.0 Silicon						
Si-Cr-Mo	90.5	89.2	. ..	89.0	90.0	90.0
Si-Cr-Mo 2½	94.0	92.0	....	90.8	....	87.8
Steels With 0.50 Max. Silicon						
0.50 Mo	67.0	....	64.0	60.5	63.8	67.8
1 Cr + Mo	89.0	....	87.0	81.0	....	79.5
2 Cr + Mo	85.5	....	85.8	84.8	84.0	85.8
4-6 Cr + Mo	92.0	....	91.0	92.0	88.8	91.0

* Specimens smaller than standard; 0.365″ square with 0.050″ V notch.
Note: Creep tests conducted for a minimum of 1,000 hours and each reported value is the average of four tests, that is, duplicate tests from two creep specimens.

pronounced. The tests at 1000 and 1100° F. were without an appreciable effect, while those at 1200° F. caused a decrease in the room-temperature ductility of the lower-chromium and lower-silicon steels.

On the basis of these results it is to be concluded that insofar as the room-temperature tensile properties are concerned the creep tests at 1000, 1100 and 1200° F. exerted no pronounced detrimental effect on any of the 11 steels, although the steels containing the higher amounts of chromium and silicon were the most stable.

Impact Resistance of Completed Creep Specimens

The room-temperature Izod impact resistance of the completed creep specimen, given in Table 6, indicate that, in the case of the steels containing up to a maximum of 1.0 percent silicon, the creep tests at the temperatures considered had no marked influence on the shock resistance, regardless of the chromium content.

With the 1.0 to 1.5 percent silicon steels the influence of the creep tests varied depending on the chromium content. In the absence of chromium, the creep tests at 800 and 1000° F. had no appreciable effect, while those at 1200° F. caused a pronounced increase in the resulting room-temperature impact resistance. In the presence of 1.0 to 2.0 percent chromium the creep tests were without influence while with a chromium content in excess of 2.0 percent the creep tests at 1100 and 1200° F. lowered the impact resistance. The minimum value obtained, however, was 60.0 foot-pounds, which is very ample for commercial applications.

These results indicate, therefore, that the combined action of stress and time at temperatures of 800 to 1200° F. does not influence in a detrimental manner the resulting room-temperature impact resistance of any of these steels.

Hot Ductility of Prolonged Stress-Rupture Specimens

The total elongation of the specimens which required the maximum time for fracture in the stress-rupture tests at each of the temperatures is given in Table 7, together with the time period.

With one possible exception, all of the steels containing 1.0 to 1.5 percent silicon possessed a high ductility under the combined influence of time, temperature and stress, regardless of the chromium content. The exception was Si-Cr-Mo 1 steel at 1000° F. which possessed an elongation value of 18.0 percent

TABLE 7

Hot Ductility of the More Prolonged Stress-Rupture Specimens

Steel Designation	Elongation, Percent in Two Inches of Specimens Fractured at Indicated Temperatures and Time Period, Hours											
	900° F.		1,000° F.		1,100° F.		1,200° F.		1,300° F.		1,500° F.	
	Time	Elong.	Time	Elong.	Time	Elong.	Time	Elong.	Time	Elong.	Time	Elong.
Steels With 1.0 to 1.5 Silicon												
Si-Cr-Mo 1	....	....	1505	18.0	1294	50.0	1705	57.0	....	....	....	....
Si-Cr-Mo 2	2300	42.0	1336	51.0	1548	62.0	926	63.0	....	....	....	....
Si-Cr-Mo 3	....	....	1385	52.5	2068	59.5	1920	50.7	1000	57.0	1368	27.5
Si-Cr-Mo 5	....	....	930	55.5	1044	63.5	927	75.0	2987	44.0	2268	74.0
Steels With 0.50 to 1.0 Silicon												
Si-Cr-Mo	....	....	6151	28.5	....	....	4000	46.2	1352	29.0	....	..
Steels With 0.50 Max. Silicon												
1 Cr + Mo	....	....	....	....	1188	31.5	1550	33.0	....	....	....	....
4-6 Cr + Mo	....	....	1603	48.0	1452	20.5	2711	33.5	5394	22.0	890	51.0

after a fracture time of 1500 hours. If, however, this ductility value does not continue to decrease as the fracture time is further extended, it would be ample for commercial applications.

Likewise the single steel considered with 0.50 to 1.0 percent silicon possessed good ductility at each of the temperatures. The same was also true of the 0.50 max. percent silicon steels at 1000, 1200 and 1500° F. However, at 1100 and 1300° F. the values for the 4-6 Cr + Mo steel were relatively low, being 20.5 and 22.0 percent, respectively.

At each of the temperatures, with the exception of the one case already noted, the high-silicon steels possessed the maximum hot ductility values and especially is this true with those steels containing the larger amounts of chromium. This increased degree of hot ductility is believed to be closely related with the higher surface stability of these steels under the given test conditions.

Metallographic Structures of Completed Creep Specimens

A complete metallographic examination was made of all the specimens, both before and after the creep tests. Space will not permit the inclusion of all the resulting microstructures, but they can be classified into two types, and an example of each is given, at a magnification of 1000 diameters, in Figure 13.

The microstructures of the carbon-molybdenum steel are representatives of those steels which, in the original annealed condition, contain pearlite in definite areas. This pearlite is not necessarily lamellar and, in fact, in this particular case, it can probably be best described as sorbitic pearlite.

The creep tests at 900 and 1000° F. have had no visual influence on the resulting microstructures of the carbon-molybdenum steel. These at 1100° F. have caused a slight degree of spheroidization, but the pearlite still exists in definite areas, no appreciable diffusion or migration having occurred. After the creep tests at 1200° F., however, not only has considerable spheroidization taken place, but the spheroidized carbides have increased greatly in size, due to diffusion and migration, and many of them are located within the grain boundaries.

The microstructures of the Si-Cr-Mo 2 steel are representative of those steels which, in the annealed condition, contain pearlite in the spheroidized condition. Consequently the creep tests do not have as pronounced an influence on the microstructure of these steels. In fact, in this particular case, any changes in structure, even after the creep tests at 1200° F., are very slight and hardly detectable. Some growth has probably occurred in the spheroidized carbides and this would be more pronounced at temperatures in excess of 1200° F.

The original microstructure of these steels is more dependent on the chromium content than on the silicon content. Regardless of the silicon content, the pearlite occurs in definite areas and is not highly spheroidized in those steels containing no chromium. In the presence of 1.0 to 1.5 percent silicon the addition of 1.0 percent chromium is sufficient to produce the second type of carbide formation, that is, the highly spheroidized type. With the lower amounts of silicon, however, a chromium content of 2.0 percent is required to produce this change. Since the steels in which the pearlite originally exists in the spheroidized state undergo the smaller structural changes during the creep tests, it follows that the addition of chromium, or of silicon in excess of 1.0 percent, increases the high-temperature structural stability.

Metallographic Structures of Prolonged Stress-Rupture Specimens

As in the case of the completed creep specimens a complete metallographic examination was made of each of the more prolonged stress-rupture specimens. Space will not permit the inclusion of all the resulting microstructures, but two representative series are included in Figures 14 and 15, one representing a steel with relatively low surface stability at the more elevated temperatures, and the other a steel with high surface stability.

In both of these figures microstructures are included both of the actual fracture and of the surface at a distance of approximately 1 inch from the fracture. All the microstructures are at a magnification of 100 diameters.

Figure 14 shows the microstructures for the 4-6 Cr + Mo steel at temperatures of 1000 to 1500° F. inclusive. Insofar as the fracture is concerned it will be noted that the 1000° F. specimen possesses a severely strained and distorted structure in the vicinity of the fracture. As the temperature of test is increased, recrystallization becomes more pronounced, and at 1300 and 1500° F. grain growth has occurred. At the higher temperatures the fracture is distinctly intergranular and the same is also true at 1100 and 1200° F. under higher magnifications.

This steel shows slight general oxidation at 1000° F. and severe general oxidation at temperatures of 1200° F. and higher. At 1100° F. the general oxidation is relatively slight but rather pronounced localized attack and pitting has occurred. This probably accounts for the relatively low ductility which was obtained at 1100° F.

All of the low-silicon steels as well as the higher-silicon steels with low chromium content possessed microstructures of the same type as those shown in Figure 14 for the 4-6 Cr + Mo steel insofar as the type fracture and general oxidation was concerned.

Figure 15 shows the corresponding structures for Si-Cr-Mo 5, a steel possessing a high degree of surface stability at temperatures up to 1300° F. Little, if any, general oxidation can be observed at either 1000, 1100, 1200 or 1300° F. In fact, even at 1500° F. this type of attack was not pronounced. However, slight localized attack, resulting in pitting, starts at 1300° F. and becomes more pronounced at 1500° F. The ductility was not influenced by this attack at 1300° F.

The microstructures of the fracture are somewhat similar to those of the 4-6 Cr + Mo steel except the grains are more severely strained and distorted at 1100 and 1200° F. Again, however, the fracture is distinctly intergranular at 1300 and 1500° F. and also at 1200° F. under higher magnifications.

These microstructures show that chromium by itself, in amounts up to 5.0 percent, is not sufficient to produce a satisfactory degree of surface stability at temperatures of 1200° F. or higher, under the given test conditions. The addition of 1.5 percent silicon, however, to the 4-6 Cr + Mo steel imparts high surface stability at 1300° F. and fair stability at 1500° F.

CONCLUSIONS

On the basis of the results presented it is apparent that too broad conclusions are not in all cases permissible with respect to the effect of variation in the

[*Continued on page 86*]

Safety in the Design, Construction and Maintenance of Combination Cracking Units

PART 1

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SAFETY records in the petroleum refining industry disclose, over the last decade, a marked decline in the rate of accidents and fatalities. This is a fact of great importance. What this increase in safety in the industry means in terms of money cannot be determined; there is no monetary scale for evaluating human health and life. Nevertheless, that the notable decline in industrial accidents is of great economic significance to companies and to employees, and that it bolsters the morale of employees, is beyond question. Fewer accidents mean a reduction in loss of equipment and production through forced shut-downs, as well as loss of employment because of disablement.

IN the refining industry the growing use of combination units naturally creates interest in the subject of safety concerning this type of equipment. A combination unit is simply a closely integrated aggregation of refining units, each of which performs in step with other elements of the plant, some particular "unit operation," such as distillation of a crude, cracking of heavy reduced crude and gas oil into gasoline, removal of undesirable constituents from raw gasoline by treating, or polymerization of light gases to high anti-knock gasoline. Before the development of combination units these and other operations were performed in separate pieces of equipment, such as distillation, cracking, treating, stabilizing and gas-recovery units. The combination unit has developed out of a need for improved quality of products and reduced manufacturing costs made possible through closely integrated operation.

Along with the combination unit has come the era of high pressures and temperatures. Also, in recent years the problem of corrosion has assumed greater importance, partly for the reason that corrosion carries with it more hazards when associated with high temperatures and pressures. Combination units may embrace processes not in use in earlier years, such as polymerization of gaseous hydrocarbons to gasoline or conversion to gasoline of hydrocarbon gases while in contact with heavier liquid materials —called reversion. These and other processes of recent development may require temperatures and pressures impracticable 10 years ago or regarded as very dangerous. Finally, the combination unit involves the continuous and well regulated flow of heat and materials among its component parts. Larger than its individual elements the combination unit possesses more points at which the question of safety may arise. This is by no means declaring that the combination unit is inherently hazardous. Experience shows that it is not. What is true is simply that the combination unit, like any other piece of equipment, is safe if soundly designed, properly constructed and correctly maintained and operated.

From the standpoint of volume of oil present in the system the combination unit is safer than some types of individual units. For example, the volume of oil carried in a tubular furnace of a combination unit is much smaller than the volume present in a shell still. This means that in the event of a furnace failure the amount of oil discharged into the fire box of a combination unit is likely to be considerably smaller than that which would flow into a shell still fire box. Safety during operation is promoted in another way. The absence of intermediate storage tanks is one characteristic of a combination unit. This reduces, of course, the chance that a body of oil during processing will become ignited from any cause and start a costly fire.

As to construction and maintenance it may be said that the problems of safety affecting combination units differ little, if at all, from those concerning other types of equipment, as will be subsequently indicated. It is principally in the field of design that combination units, relatively complicated in their interrelated operation, and often involving high pressures and temperatures, may seem worthy of special attention.

SAFETY IN DESIGN

Safety in operation begins with safety in design. One of the early steps in the design of a combination unit is the location of the various sections of the equipment. A large unit generally has elements operating under widely different conditions of pressure, temperature and character of raw material being processed. This calls for planning the layout of the equipment with a view to maximum possible reduction of fire hazards. Where space permits, some segregation of high-pressure, high-temperature equipment (such as furnaces and reaction chambers), gas-compression plants, light-oil treaters and accumulators or storage tanks for inflammable volatile materials is advisable. Combination units may include all these pieces of equipment. Furnaces should be kept as far away as is practicable from possible

[1] Presented before the annual meeting, Petroleum Division, National Safety Council, Chicago, Illinois, October, 1938.

sources of a conflagration. It is good policy to separate or otherwise protect containers of volatile oils or inflammable gases from high-pressure processing equipment.

Towers should not be set so closely together as to increase the probability of fire spreading among them. Furnaces should not be placed close to towers. Gas plants and treaters should be set apart from the main cracking equipment. Sufficient spacing should be left around pump and control rooms to allow the easy escape of men in an emergency. Pumps within pump houses should be properly spaced for safety and easy access.

Safety in design is predicated upon extensive knowledge of the numerous materials of construction now available to the refiner. Obviously, equipment should meet as far as possible the most severe conditions it might reasonably be expected to encounter. It should be able to meet these conditions as long as it is to remain in use, whether for months or years. In other words, there must be confidence that materials can resist adequately the various weakening influences met constantly and occasionally in refinery practice. Factors of safety as used in design are dependable to the degree that design calculations are based upon trustworthy data. Extensive and intelligent testing of materials is an absolute necessity in the design of modern combination units. Will this material bear up properly under the load to be laid upon it? Will this metal, or that alloy, present adequate resistance to the weakening effects of corrosion and erosion, to shock, to temperature, to pressure? Will it weld properly? Such questions have to be answered with assurance before there is confidence that a material selected for a given function will perform safely. The physicist, the chemist and the metallurgist must all contribute their knowledge here. Combination units utilize numerous metals and metal alloys having widely different properties to meet conditions encountered in practice. A material suitable for high temperatures may be dangerously brittle at very low temperatures. A metal sufficiently resistant to heat and pressure may be the easy prey of corrosion. Foolish indeed would be the designer of equipment who specified a material without considering its probable response to all conditions it would be likely to encounter. He must know its properties. Furthermore, the man in the construction shop must be familiar with the type of materials with which he is working. A man trained in work upon one type of metal may need new training when he is working upon material of a different type. For instance, a man familiar with the welding of carbon steel may require additional instruction and practice when welding alloy materials.

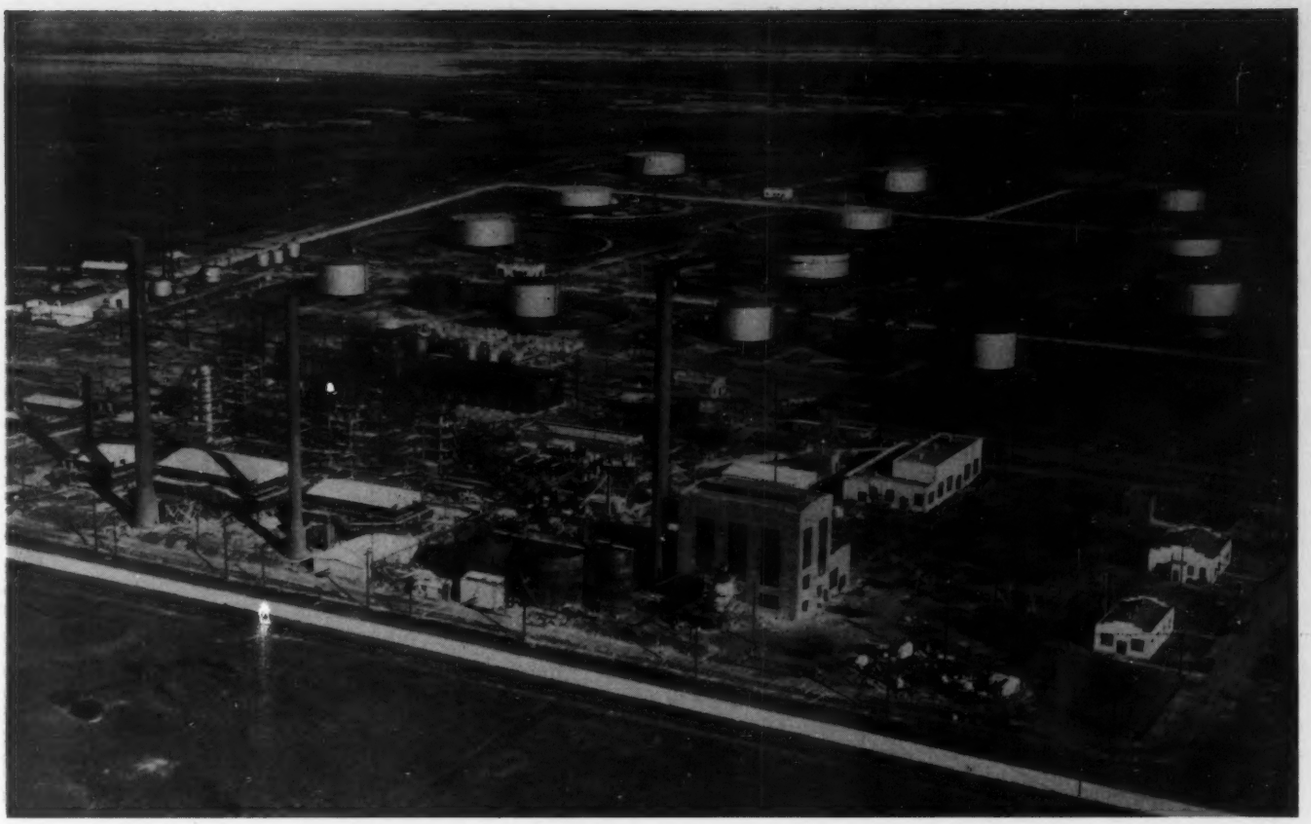
Approaching the design of the various elements of a combination unit, we may first discuss safety in the design of furnaces. The modern pipe heater may involve oil temperatures up to 1100° F. and pressures of over 2000 pounds per square inch. The material being heated might be extremely inflammable, such as a liquefied mixture of gases. It may carry with it an impurity that is highly corrosive to ordinary steel. Obviously, considerable care has to be devoted to the design of tubular furnaces to reduce or eliminate the possibility of trouble during operation and to cope most successfully with trouble if it does occur.

Corrosion is, of course, one of the chief enemies of furnaces in the refining industry. In recent years corrosion has been an increasingly troublesome problem. One reason has been the development of acid treating of wells to increase crude production; acids used in wells tend to increase corrosiveness of crudes. Another reason for the growth of the corrosion problem is the increase in the amount of high-sulphur crudes to be processed. High sulphur often goes hand in hand with severe corrosion. Furthermore the severity of corrosion may be considerably increased at the high temperatures regularly employed in modern refinery furnaces. Protection of furnace tubes and fittings against failure from corrosion may take the form of generous factors of safety applied to design calculations. Metal walls made considerably heavier than operating pressures require, may be reasonably secure against failure through corrosion. This, of course, is an expensive procedure, involving as it does the constant payment of tribute to corrosive action. Yet it must be followed unless other means are used to combat the evil.

One of the best weapons in the fight against corrosion is corrosion-resistant alloy metal for tubes and headers. The alloy may be used throughout or used as a lining integrally bonded with ordinary steel. The first cost of good alloys is higher than that of carbon steel, but this may be easily offset by lighter weights required and by better assurance against failure, fire and fatalities. High-temperature-cracking systems and polymerization equipment frequently demand the use of alloy furnace tubes. The need for heat-resistant tubes at temperatures above 1000° F. may dictate the employment of alloys, entirely aside from the question of corrosion, particularly near furnace coil outlets. It is fortunate that the metallurgical laboratories have kept pace, in their development of alloys, with requirements of recent refining processes now embodied frequently in combination units. Under numerous circumstances the old materials simply will not perform safely.

Protection from the weakening effects of high temperatures must extend to other parts of the furnace than the tubes. Concrete work has to be sheltered from the disintegrating influence of heat. Ducts carrying cool air or water are sometimes employed in design to keep temperatures at safe levels. Insulation in some form is another means of protecting concrete. Concrete, where employed as flooring, needs to be kept comparatively cool not merely for its own protection. The soil beneath is itself susceptible to excessive heat and if it carries an appreciable percentage of water, drying out may weaken it and cause serious settling of the furnace and produce stresses in the structure threatening to its integrity.

Various effective devices are employed in designing a furnace and its appurtenances to facilitate the fighting of fires, reduce their damage to a minimum and protect operators. Part of the standard equipment of a furnace is steam piping enabling operators to turn a blanket of steam into the compartments or boxes surrounding the tube headers, where fires due to leaking joints may occasionally develop. A cloud of steam will often smother a header-box fire. Infrequently some inert gas other than steam is used, but steam, available in all refineries, is in general use. It is wise to provide for the remote control of header-box steam, since a bad leak conceivably could prevent the opening of a valve in the steam line close to the header-box. Steam lines to permit filling of the furnace fire box with steam are also used, though not so extensively as lines to header boxes.



View of a combination unit, including polymerization plant, showing general layout, together with power house and tankage.

Blowdown lines to permit the emergency emptying of a furnace coil into a water-sprayed blowdown stack are also a necessary part of the fire protection equipment for furnaces. Such lines enable operators to discharge the contents of the coil in case of fire. Automatic valves, air, steam or hydraulic—operated with safety from easily accessible points—are ordinarily used. Needless to say, the capacity of the blowdown system should be ample, so as to permit a rapid clearing of the coil. The blowdown stack, which is regularly situated at some remote point in the refinery, is commonly fitted with spray rings on the inside to permit discharge of quenching water to cool hot oil, and with steam for snuffing fires. It is also important that the discharge piping should be so arranged that oil will not remain in any low point or "pocket" of the coil and thereby promote formation of coke.

Steel stacks are lined part of the way up on the inside with firebrick that is generally second hand. Water rings, perforated so as to permit spraying the stacks on the outside with water, are ordinarily installed. These are precautions taken to protect the steel stack in case of fire, and prevent its collapse due to heat.

Iron explosion doors are commonly installed in furnace walls. These coverings over small apertures are hinged at the top and normally remain closed by their own weight. Their purpose is, in case of a sudden rise of pressure within the furnace box from any cause, to fly open and thus release pressure that might otherwise destroy the roof or walls. Designers usually establish the number of explosion doors in proportion to the cubical volume of the furnace box.

Safe furnace design calls for the provision of adequate steel walkways and stairs or ladders about the setting. At times walkways should extend entirely around the furnace, so as to give the operators every chance to escape in case of fire. Along the outer edges of these walks should be attached low metal strips or toeboards. One function of such strips is to prevent tools or other loose objects from being dropped down upon men below. Another function is to stop the sliding foot of an operator who has slipped and is about to fall to the ground. Walkways should be further protected by handrails. Likewise ladders and stairs leading to walkways should have railings.

Instrumentation is, of course, an indispensable means of keeping furnaces operating safely. Inasmuch as this applies with equal force to the other elements of a combination unit, the subject of instrumentation will later be discussed separately.

With reference to safety in the design of vessels in use on combination units, it may be pointed out at once that the same problem of corrosion discussed in connection with furnaces is also present here. Corrosion arising from sulphur compounds or the hydrolysis of some chlorides may seriously affect the strength of towers, accumulators and heat exchangers. In some cases the raw feed stock to a combination unit can be partially freed of its corrosive agents before entering the unit. The settling out of salts and the neutralization of corrosives susceptible to such treatment at least partially solves the problem of corrosion beforehand. In some cases such procedure is practicable.

The treatment of crudes, however, may prove impracticable. What then, is to shield metal walls, often under hundreds of pounds of pressure and at temperatures over 900° F., from the incessant, insidious attack of corrosion? One means of combating corrosion is the use of corrosion-resisting, non-metallic linings for vessels. When made of suitable materials

Welded pressure vessel after failure at 3200 pounds per square inch hydrostatic test pressure, five times normal working pressure.

and properly applied, such linings halt or decrease corrosion. Their period of usefulness, however, may be comparatively short, particularly if the vessels are exposed to shock and vibration. The frequent result is cracking of the lining and the seepage of corrosive materials through the rupture. Where linings of this type are employed it is essential that they be regularly inspected.

The use of alloy vessels, where the saving due to their use is greater than the cost of periodically replacing ordinary steel equipment, is an effective answer to corrosion trouble. Alloy heat-exchanger tubes are often mandatory where failure of thin metal walls would create a dangerous situation. Fortunately, the development of alloy linings integrally bonded with ordinary metal walls has considerably reduced the cost of alloy protection against accidents resulting from corrosion. These dependable linings are now applied to a wide variety of vessels.

After the material for a vessel has been selected and the vessel has been fabricated, it may be advisable to relieve metal stresses after the completion of welding. This precaution is worthwhile particularly where the vessel is to be used for high-temperature, high-pressure service. The relieving of stresses at welded seams by controlled heating and gradual cooling is a safeguard against subsequent failure of a joint. The shells of heat exchangers as well as larger vessels may require this treatment.

An X-ray examination of seams is another precaution to assure safety in welded vessels. X-rays tell the story. Hidden folds, cracks and other defects not visible to the unaided eye are revealed before they have a chance to produce a rupture during operation. If a vessel is to function under high pressure and temperature a thorough X-ray examination is well worthwhile.

The erosion of metal surfaces occasionally becomes a matter of concern. In some cases there may be anticipated marked erosion, or wearing away, of the walls of vessels facing nozzles through which fluids are entering the chambers at high velocity. Erosion is likely to be severe if the fluids carry an appreciable amount of suspended gritty matter. This condition may call for the placing of deflector plates in positions where they receive and dissipate the full force of the incoming fluid. There is another method of meeting the problem. If it is practicable to arrange piping so as to allow a fluid at high velocity to enter a vessel tangentially it will sweep around the curvature of the wall rather than impinge directly against it.

The presence of appreciable quantities of water in oil entering vessels, or the use of spray steam, where conditions favor the gradual accumulation of water in pockets, may present a problem in design. This arises where there is possibility of the freezing of entrapped water when the combination unit or some portion of it is not in use, resulting in a rupture of equipment occasioned by expansion of water after freezing. Draw-offs for the removal of water usually serve in such cases. Vents should be installed in vessels to permit ingress of air as water is drawn off, if it is likely that water will not otherwise flow out of the equipment.

Safety valves on vessels constitute one of the foremost means of securing safety during operation. Regardless of foresight and precaution on the part of operators, there is always the possibility that the unlikely will happen. It is unlikely that sudden and dangerous rises in pressure will occur in properly designed, well managed equipment, but it is well to provide for them.

There are various conditions under which unintentional increases in pressure might develop. Suppose the cooling water supply to a tubular condenser were to fail. As the water capacity of this type of condenser is relatively small, an interruption in the water supply, if long continued, will cause the condensation of incoming vapors to cease. This in time may result in the building up of pressure in a tower above the safe operating pressure.

Abnormal pressures may also develop through failure of the reflux supply to a tower. Where the temperature of vapor issuing from a tower is controlled by open reflux or cooling coils, failure of the refluxing medium will produce an excessive volume of effluent vapor. If the receiving system into which the vapor flows cannot handle the excess, an upsurge of pressure will occur.

A third cause of abnormal pressures is the inadvertent closing of a valve or the plugging of a valve in a line. A careless operator or a defect in a valve may be the cause of a dangerous condition.

There are other conditions which may set up excessive pressures either in or out of operation, such as heat from the sun, from adjacent hot equipment, from hot fluids flowing out of a break in an exchanger tube and from external fires.

SAFETY VALVES

The above contingencies call for the use of properly-designed safety valves. There are numerous towers on combination units on which the use of safety valves is justified. Whether a valve is to discharge into the atmosphere or into a blowdown sys-

tem must be determined by circumstances. For instance, where only the release of light vapors is likely, the discharge of these vapors directly into the air with steam may be permissible. On the other hand, if an appreciable discharge of liquid from a valve can be anticipated, it probably will be advisable to have the safety valve discharge into piping leading to an isolated blowdown stack to avoid a fire. It is essential that no valve be permitted to release vapors or liquids if an uncontrollable ignition of the material is likely to result.

The use of safety valves is not always confined to large vessels like evaporators and fractionating towers. Valves may be found necessary on heat exchangers. Safety valves are often installed on the shell side of exchangers for protection against excessive vapor pressure. Liquid-expansion valves may be installed on the tube side of exchangers as further protection.

The insulation of vessels is a regularly used and necessary form of protection against collapse or explosion of equipment during fires. Mineral wools, brick and concrete are the materials ordinarily used. Insulation shelters metal from the softening effects of heat and reduces the vaporization of liquids in vessels during fires. The insulation of vessels should extend to their steel supports, which, like the vessels, may be seriously weakened by fire. The commonly used insulating materials for supports are brick and concrete.

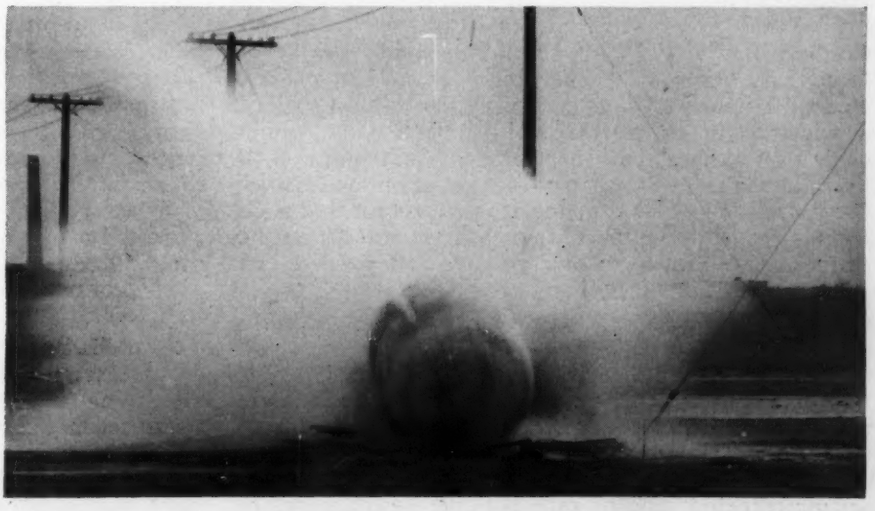
Structures allowing the quick escape of operators or workmen at the outbreak of a fire should always be provided around vessels on combination units. Railed stairs, ladders and walks greatly contribute to safety. Ideally, they should be so arranged as to enable operators to descend readily from elevated positions to the ground, or to escape quickly from equipment-filled areas on the ground level. Some refiners install chutes to permit men to slide quickly down from towers and other elevated structures in case of fire. An alternative to the use of chutes is the installation of slide wires, which serve the same purpose.

Fire walls, usually of concrete and from one to three feet high, are ordinarily regarded as necessary. Constructed around individual components of a combination unit, they serve to prevent the spread of oil over a large area in case of accidental discharge of the fluid. In this manner the exposure of equipment to fire may be prevented. Policy varies with respect to the amount of equipment to be encompassed by fire walls and the height of the walls. Vessels for unusually high pressures may be separated from other equipment by walls of considerable thickness and 8 or 10 feet high. Such height is primarily to protect operators and equipment in case of an explosion, and may not be necessary all the way around the high-pressure vessel.

PUMP INSTALLATIONS

In addition to furnaces and vessels there is the subject of pumps and piping to be considered from the standpoint of safety. One of the characteristics of combination units is concentration of equipment in a relatively small area. This feature makes practicable the location of pumps at one or two points. The concentration of pumps makes for greater safety in operation for the reason that operators can attend more quickly to the pumps. Furthermore, pumps can be better protected from fires by being installed in properly located houses. Refineries differ on the question of inserting windows in these houses in walls directly facing cracking equipment. When windows are inserted, there is always the possibility that the force of an explosion or a blast of flame will break through the windows and injure the operators inside. For this reason, it is the better practice not to install windows in walls facing cracking equipment. It is often the practice, where high-pressure hot-oil pumps are installed with other pumps in the same pump house, to isolate the hot pumps with partitions. This is a precaution for protecting operators and equipment. Various means are available for coping with the fire hazard in pump rooms. Enclosed rooms in which inflammable vapors would be likely to accumulate are often provided with forced ventilation for constant discharge of gas. Pumps and compressors handling very volatile liquids and vapors may require the installation of collecting systems to remove gases escaping from such equipment. For wholly enclosed pump rooms the use of inert gases to displace air during a fire is effective. Steam is commonly employed. Carbon dioxide is used by some refiners. It is obvious that suffocation of fires in this manner is impracticable for pump rooms with open sides. The installation of remote control for pump drives is good practice. This enables operators to maintain control over pumps if a fire occurs in a pump room. Some refiners make a practice of installing safety valves on turbine exhausts. Sometimes these valves are merely warning whistles which sound when the turbine exhaust steam pressure exceeds a certain point.

Spare pumps are a necessity in many cases, since



Welded pressure vessel failing under hydrostatic test pressure of 3200 pounds per square inch, which is five times normal working pressure.

they insure continuity of operation in case of breakdown of regular equipment. It has been pointed out that failure of the supply of reflux to a fractionating tower may create a dangerous rise in pressure. Spare reflux pumps are very advisable. In general, particular operating conditions dictate whether a spare pump is required in a given situation. It is highly desirable to restrict the number of regular pumps to be spared by a single pump. Generally the number is not more than two. The reason, of course, is to reduce the chance that a spare pump might be called upon simultaneously for two different services. Where it is practicable spare pumps should have electric drives if the regular pumps are steam driven, and vice versa. This system guards against complete paralysis of pump service if the electric power or steam supply should fail. Under some conditions it may be practicable and advisable that the change from regular to spare pump operation be automatic. In other circumstances a manual change may be permissible.

PROTECTION OF PIPE

Piping, which with pumps makes up the fluid transmission system for the unit, has its own problems of safety. For one thing, the same troubles visited upon furnaces and vessels by corrosion also affect piping. The means for reducing pipe corrosion are similar to those employed elsewhere on the unit, although non-metallic linings are little used. The thinning of pipe walls by erosion is most practicably reduced by avoiding the use, as far as possible, of sharp pipe bends for oil moving at high velocity.

Where there is likelihood of thinning of metal at pipe bends, tell-tale or test holes are often used. These are holes of small diameter drilled into the pipe at the point where the greatest thinning is anticipated. Usually the are drilled to within a distance of the inner wall of the pipe equal to the thickness of the corrosion allowance. When this thickness is eaten or eroded away the fact is announced by leakage through the hole. Tell-tale holes have disadvantages pointed out in the section devoted to safety in maintenance.

Considerable lengths of piping at high temperature require some device to permit expansion. Otherwise a pipe may break at a joint or overstress a connection with a vessel or pump. Expansion bends or loops may be used to absorb elongation due to heat. Packed expansion joints are used for some types of service, although the possibility of leakage limits their use. Where there is likelihood that piping will probably vibrate to a considerable degree because of the movement of fluid inside, it is important that such piping be firmly supported so that vibration may be reduced to a minimum or eliminated altogether. Excessive vibration in piping tends to open up fissures created by corrosion and so to accelerate the weakening of the pipe by corrosive action.

It is good practice, especially for service near equipment in which a fire might develop, to insulate piping for fire protection. Likewise it is advisable to insulate metal supports for piping, particularly those for heavy lines or groups of lines. A fire may weaken an unprotected pipe or pipe support to the point of collapse and breakage, thus adding fuel to a conflagration or paralyzing a line used in fire fighting. An alternative to the insulation of overhead piping is the use of pipe trenches. A disadvantage to trenches is that if the piping is crowded, inspection tends to be difficult. Furthermore, there is the chance that oil will accumulate in such trenches and increase liability of fire and explosion.

CONTROL INSTRUMENTS IMPORTANT

Instrumentation on combination units is an important factor in the promotion of safety. This, in general, is true for other types of refinery equipment. It can confidently be asserted that numerous refinery fires and explosions have occurred through lack of, or defects in, control instruments. Unless automatic regulating instruments are dependable they are more of a hazard than simple manual control intelligently exercised. Aside from the subject of automatic regulation a refining unit certainly should possess enough temperature, pressure and metering instruments to provide the operators constantly with information sufficient to maintain safe operating conditions. What is the temperature? What is the pressure? What is the rate of flow? Where is the level of the liquid in this vessel? Correct answers to such questions may mean the difference between good operation and catastrophe.

Combination units offer a good field for the application of instruments. In these units there is a close interrelation among numerous refining processes, which requires regularity in the maintenance of pressure and temperature conditions, and rate of flow of many streams of liquid and vapor. It is often the case that considerable variations in operating conditions not only will adversely affect products, but also will become dangerous. Properly installed and used, however, instruments make even the most complicated combination unit dependable to the full degree of safety that structural design affords.

Safe instrumentation on a combination unit is assisted by the fact that the principle of remote control can be employed. Most of the instruments are grouped in a central control room, generally placed at some safe point and constructed to resist explosion and fire. If the control room is closely adjacent to cracking equipment, it is advisable that no windows be placed in walls confronting the equipment. This is a precaution to protect men on the inside of the room from the force of an exterior explosion, if any should occur. On the modern combination unit operators do not spend a large part of the time walking around to read instruments and make adjustments. Instead we have remote control in a well-protected room. This means that operators stand less chance of being trapped at some point of the equipment by a fire or hurt by an explosion. It also means that they can, in case of fire, exercise a considerable degree of control over the unit without exposing themselves to danger.

An added degree of protection for the instrument room is secured by the practice of remote control of regulating instruments used for high-temperature, high-pressure service, rather than bringing the piping from the equipment directly into the control room. Instrument piping looks deceptively harmless in most cases. A careless operator may open a small line only to encounter a hot stream of oil perhaps flowing under a pressure of hundreds of pounds.

Remote control is used to minimize the possibility of such an occurrence and to reduce the chance that a high-pressure instrument line may break in a control room. It is essential in design work to determine, in the event of a failure of a flow-control mechanism to operate, whether greater safety lies in permitting flow to proceed unhindered or stopping it altogether. Circumstances must determine which alternative is elected. For example, it is common practice to arrange that the flow of oil through a pipe furnace shall continue in the event of a failure of the flow control mechanism to work. This prevents burning and coking of the furnace tubes.

If it is impracticable to provide for remote control of regulating instruments as outlined above, there is one precaution which may be taken to warn operators against inadvertent opening of a high-pressure, high-temperature instrument line entering an instrument room. This consists in painting the line and its fitting red or some other distinctive color.

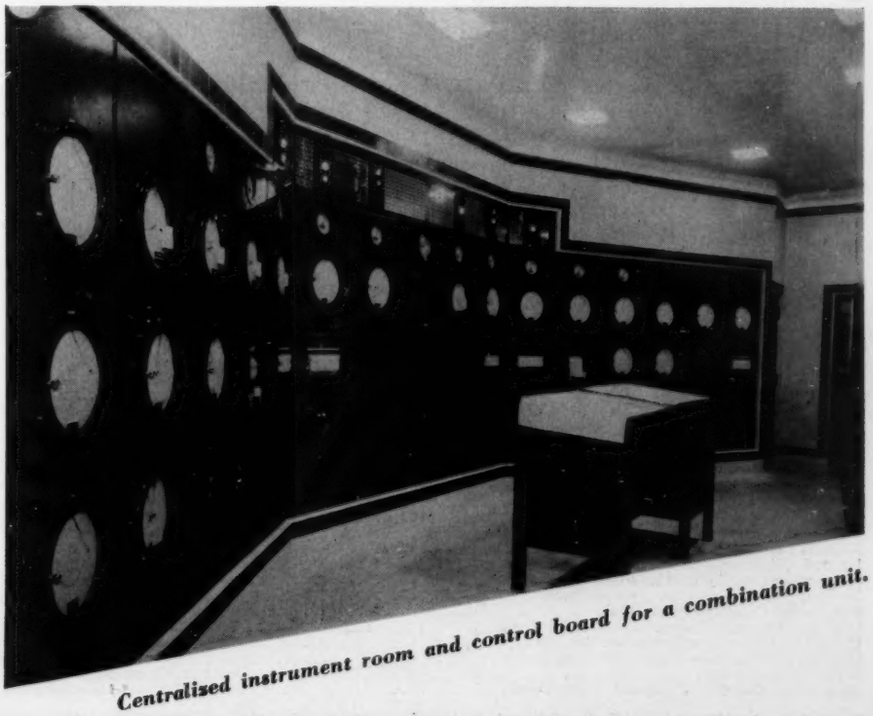
The types of instruments to be used for certain purposes are numerous. Their selection depends on operating conditions, and is outside the scope of this paper. It is proper, however, to point out that their chief functions are to indicate momentary operating conditions, to make continuous records of conditions and to control conditions. In the performance of these functions reliable instruments can greatly promote safety. They must be well designed and must be properly protected and serviced regularly. Gauge glasses should have bars, netting or other means of protection against breakage. Many instruments are operated by air or electrical power. Good design of an instrument installation requires that, if air is used, the air be kept clean and dry and the supply dependable. Oil or water vapor may clog an instrument. Water vapor may cause a failure through freezing in the winter. Small connecting piping between instruments and equipment should be insulated against fires or cold weather. Pressure gauges connected by piping with furnace transfer lines or other equipment where there is danger of coking of the connecting pipe should be assured of good operation. This can be done by supplying through the pipe a constant small stream of light oil, such as gas oil, which discharges into the main body of oil in the equipment. This stream usually prevents coke formation.

ELECTRICAL EQUIPMENT PROBLEMS

Electrical equipment has its own particular problems. First of all, there is the need of a constant supply of power to actuate instruments. Some large combination units are provided with spare generator sets to maintain the operation of instruments and lights in case of failure of the regular power supply. Provision is made for an automatic switching of instruments and lights to the emergency supply. Electrical switches used where there is a possibility that inflammable vapors will be present, should be of a type to prevent explosions from arcing. Conduits for carrying wires should be sealed to avoid the possible transmission through the conduits of inflammable vapors. It is sound policy to protect instrument wiring from destruction by fire by the use of metal or other durable conduits. Motors and generators, if operating in an atmosphere of inflammable vapors, may cause fires by sparking. The use of suitable spark-arresting devices on such equipment is highly advisable. Systems for maintaining a non-explosive atmosphere in rooms containing electrical equipment in the presence of inflammable vapors always contribute to safety. The grounding of equipment is necessary to prevent the accumulation of static electricity, which might cause a discharge of sparks.

There is hardly need to devote a separate section to the design of a fire-protection system for a combination unit. The subject of fire protection has been largely covered in those sections dealing with the safe design of furnaces, vessels, pumps and lines and instrumentation. The use of steam and other inert gases has already been discussed. Combination units, like other refining equipment, are regularly serviced by water lines which may or may not be supplied by special high-pressure pumps to make the fire-fighting system independent of the operating system. Foam systems are often used. These may be either in the form of permanent installations or portable sets to be wheeled to the site of the fire. A good device to make water and foam lines and connections easily distinguishable from other equipment is that of painting the fire-fighting equipment one or more distinctive, bright colors. Quenching sprays, which enable men with clothing on fire to shower themselves quickly with water, and fire blankets, which serve much the same purpose in extinguishing fires on clothing, should be installed close at hand for use of the operators. Likewise should ointments and other first aid supplies be furnished at convenient locations.

(To be continued)



Centralized instrument room and control board for a combination unit.

Gas-Distillate Production

In South Texas Brings

Gasoline Plant Construction Program

EARL S. POST

DEVELOPMENT of condensate production along the South Texas Gulf Coast is providing an aggressive natural gasoline plant and recycling unit construction program. The first two major units were placed in operation at the beginning of the year and several new plants are contemplated for 1939.

This program is the definite follow-up to several economic events, as well as the designing of successful recycling units for deep sands. These reasons are generally summed up as follows:

(1) Condensate producers are high gas/oil ratio propositions and under the present Texas Railroad Commission rulings would be shut in for gas wastage unless a market has been provided for the residue gas. This virtually eliminates the production of high-gravity distillate, or gasoline from these sands through regular separator methods unless the area has the good fortune of being close to and connected with a natural gasoline plant, or sufficient market is provided through sale of residue gas for nearby drilling rigs.

(2) Most distillate or condensate sands are low-recovery producers and are found at extreme depths, making production on a regular basis generally economically unsound. Through recycling, pressure is maintained and greater recovery is possible.

(3) Higher allowables are available for wells produced by this method. In most cases, 25 percent of the open flow capacity of a gas/oil producer is allowed, provided the gas is returned to the formation, or is sold in a legitimate market. On the basis of a crude allowable, wells may be restricted to 50 barrels per day, but as condensate producers, their production may be increased to several hundred barrels per day.

(4) Wider spacing is possible. This is the opinion of engineers on several projects, who in designing the repressuring program point out that drainage from several hundred acres is possible, where maximum recovery under ordinary production methods would be restricted to a limited sector.

(5) Numerous producing areas heretofore considered unfavorable for production and classified as purely gas reserves now become valuable. One particular instance is a large individual fee ownership upon which two wells proved several high gas, low oil producing zones several years ago. The block was dropped, being determined solely as a gas proposition. Further exploration by another company, plus the construction of a large gasoline and recycling unit has made this one of the key fields of the lower Gulf Coastal trend.

(6) High prices received for fluid and immediate demand for gasoline and distillate makes this an attractive proposition.

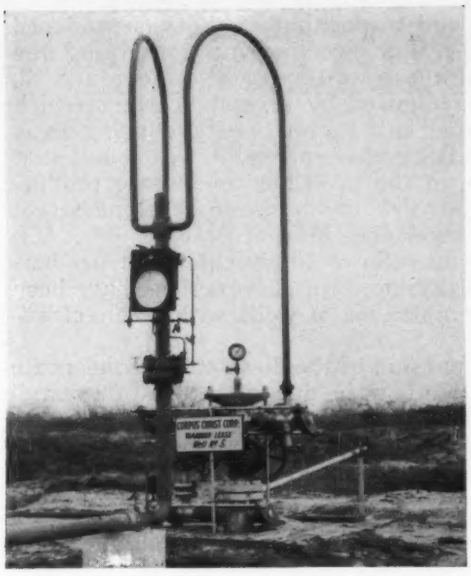
As a result of the above, it can be seen that much attention will be paid in the future to these reserves, especially those held in large units where operation of the plants is simplified. Where leases are well broken up and fee ownership is divided, complications arise in the division of royalties and damaging or aiding effects of the repressuring.

A survey of South Texas at the first of the year showed that there were 30 fields along the lower Gulf Coastal trend producing distillate or capable of producing distillate or condensate from one or more sands, and also considered likely prospects for recycling units. A number of other crude producing areas in this sector have residue gas from wells apparently adapted to processing through one of several types of gasoline units. At the beginning of the

TABLE 1

Natural Gasoline Plants Operating in South Texas January 1, 1939

COMPANY AND LOCATION	Type	Capacity, Cubic Feet Gas Pressure	Gallons
Corpus Christi Corporation, Stratton	High-pressure recycling	50,000,000	50,000
Clymore Company, Refugio	Absorption	30,000,000	25,000
Duval Gasoline Company, Benavides	Refrigeration process	1,250,000	2,000
Humble Oil & Refining Company, Heyser	Absorption	25,000,000	50,000
Humble Oil & Refining Company, Flour Bluff	Absorption	15,000,000	15,000
Manhattan Gas Company, Sinton	Low-pressure—absorption	20,000,000	20,000
Natural Gas Corporation, Aransas Pass	Low-pressure—absorption	90,000,000	40,000
Process Oil Company, Agua Dulce	High-pressure recycling	15,000,000	4,200
Southern Minerals Corporation, Corpus Christi	Low-pressure absorption	75,000,000	40,000
United Gas Pipe Line Company, Refugio	Absorption pressure	50,000,000	25,000
United Gas Pipe Line Company, Agua Dulce	Absorption and cracking	50,000,000	35,000
J. H. Webb, Chitim	Drip separator	2,500,000	700
Agua Dulce Gasoline Company, Agua Dulce	High-pressure recycling	60,000,000	60,000



year, 13 plants were operating along the lower Gulf Coast, only 3 of them being recycling units.

Prior to 1934, there were 2 plants in the territory. United Gas Company had constructed and is still operating a natural gasoline plant in the Refugio field. This is an absorption unit constructed to handle a maximum of 50,000,000 cubic feet of gas daily. Its average run has been 47,000,000 cubic feet per day with a recovery of about 2000 gallons of gasoline. The gasoline content of the gas at Refugio is from .425 to .50 gallons per 1000 cubic feet. The gas is being taken from the gas separators and residue gas is run to United Gas Pipe Line Company's trunk line for commercial consumption.

J. H. Webb was one of the first operators in the area, constructing a gas treating and trip separator plant in the Chiltim field of Maverick County, where 2,200,000 cubic feet of gas daily provides about 700 gallons of gasoline. This is the only plant off the Gulf Coast trend, the production coming from the 5600-foot Glenrose formation. Wellington Oil Company and Texas Gas Utilities Company control these reserves, the latter running the gas through its pipe line system.

Early in 1934, Clymore Production Company erected and placed into operation a combination absorption and refining unit built to handle a maximum of 45,000,000 cubic feet of gas per day, plus a number of high-gravity, excessive gas/oil ratio producers. The gas from this field averages .03 to .04 gallons per 1000 cubic feet. The oil produced is 55 gravity and runs about 80 percent gasoline of from 68 to 70° A.P.I. It was operated for some time, running 17,000 gallons of gasoline from the gas runs and about 14,000 gallons of gasoline and naphtha from the oil runs. It operated for only four months during 1934, then shut down. Later it was acquired by United Gas System and after further expansion and reworking was placed into operation. It still is producing, residue gas being run through the company's trunk line.

A number of units were constructed to handle residue gas from crude oil producers, the gas being taken from the separators and handled through low-pressure absorption or similar type plants. These units, likewise, have become popular in oil producing areas.

Parker, Foran, Knode & Boatwright, engineers of Corpus Christi, entered the Agua Dulce field in 1937 with a high-pressure separator unit, taking gas from one well and recycling it through another. The plant, operated under the name of Process Oil Company, was constructed for experimental purposes. It takes the fluid and gas from the 4800-foot sand through high-pressure separators and back into the sand through a second well with only one stage of pressure step-up. Using several million cubic feet of gas per day, the plant produces 4200 gallons of high-gravity gasoline. This sand is capable of producing considerable oil through regular separator methods.

The above company has applied to the Texas Railroad Commission for permission to withdraw fluid and gas from sands deeper than the 4800-foot sand, process the production, then return the gas to the formation. This work is being carried on in the southern portion of the Agua field where the company has the Ingram tract under lease.

Agua Dulce Gasoline Company's plant at Agua Dulce and Corpus Christi Corporation's unit at Stratton field, recently have been placed into operation.

Corpus Christi Corporation has its plant near the center of a producing block of approximately 8000 acres. The producing wells range from 4800 to 6400 feet, activities being directed to the lower zone. All of the wells are tied into flow lines to the plant, some being 8300 feet away. The oil is separated at 800 pounds pressure direct from the well. This pressure is to be stepped up to 1200 pounds shortly. The gas, after having the gasoline removed, is compressed through four 600-horsepower compressors in a single operation, being returned to the formation in one input well at a pressure of 2700 pounds. Seven wells provide the production and an eighth is used as input. The plant has a capacity of 50,000,000 cubic feet and produces nearly 60,000 gallons of fluid per day.

Designed to repressure sands at 4600 to 4800 feet, Agua Dulce Gasoline Company's unit in the Agua Dulce field, built by J. Wood Glass and Henderson Company interests, yields 60,000 gallons of fluid per day. It separates oil under a direct pressure of 1200 pounds, the residue gas being restored to the formation under 1900 pounds pressure. Twelve output and four input wells supply the plant.

The results of these plants will have an important bearing on the future of this type of development. Maintenance of the original conditions in the producing sand, which is part of the plans of these installations, is of economic importance, especially in those areas similar to Agua Dulce and Stratton where the production is a clear distillate or water-white condensate. This fluid is believed to exist largely, at the increased pressure and temperature in the formation, in a dense cloud of vapor or gas. As the pressure is decreased, condensation often results and much fluid apparently is never to be recovered in the interstices of the porous rock or sand. However, by the injection of the gas that is produced with the oil or distillate this loss in the sand may be prevented and the decline in pressure will be slight. This would mean that the greater part of the vapor would ultimately be recovered.

Along the above lines, evidence was presented at a recent litigation between Southern Minerals Corporation and Jay Simmons et al concerning the condition of distillate in the formation. Fluid produced from the 5700-foot sand in the Saxet field, together with water and gas, were experimented with by Dr.

George G. Brown, professor of chemical engineering for the University of Michigan, in his laboratory at Ann Arbor. These samples were mixed in their exact ratios as found at the separator at the well site. When subjected to a pressure of 2850 pounds and 168°F., considered the same conditions as in the well, the liquids were transformed into gas. As the pressures were lowered, the gas commenced to condense, turning into fluid when the pressure reached 610 pounds and temperature 70°F.

When a definite decision is made concerning exactly what is a condensate well, rules governing their operation can be set up. The Texas Railroad Commission took definite steps in this direction early last year by making a survey of producers apparently in this classification. On October 15, 1938, a hearing was called, its title being the classification of wells producing high-gravity, high-volatile liquids at high gas-liquid ratios, the methods of producing such wells in order to obtain the greatest ultimate yield from reservoirs on which such wells are located and the utilization and disposition of the gas produced from such wells. The first hearing concerning the classification of these wells was held February 23, 1938. This was followed by several hearings which ultimately resulted in a survey of all producing areas in Texas. In making this survey, it was found that 205 wells were in the probable condensate producing classification. For the basis of development of this list, wells producing fluid of at least 46° A.P.I. under a minimum ratio of 10,000 cubic feet per barrel were included. Since that survey, there have been a number of completions of wells within this classification.

The rapid expansion of the distillate or condensate type of production is to be one of the most outstanding developments along the South Texas Gulf Coast. Due to the apparent extensiveness of the reserves and close proximity to deep water outlet, there is little doubt but what it will be a future factor from both a producing and refining point of view in South Texas.

TABLE 2

Survey of Distillate Areas in South Texas January 1, 1939

COUNTY	Field-Prospect	Type Production	No. Sands Distillate	Range Depths Dist. Sands	Plants Operating or Proposed	Major Leaseholders
Aransas	*Lamar	Gas/Dist	2	8000–8600	None	Barnsdall Oil Company.
	†McCampbell	Crude/Dist	2	6800–7100	1	Atlantic, etc.
Bee	Beeville	Gas/Dist	1	5800	None	Houston, Magnolia, etc.
	Holzmark	Gas	1	3600	None	Several independents.
Calhoun	†Heyser	Gas/Crude	...	.....	1	Humble, Plymouth, Gulf, etc.
Duval	†Benavides group	Gas/Crude	...	.....	1	Hiawatha, Arkansas, Standard of Kansas, Humble, etc.
	†Thomas Lockhart	Gas/Crude	....	.....	None	Lockhart Brothers and E. R. Thomas Estate.
Goliad	Slick	Gas/Crude	...	.....	None	Dirks Brothers, The Whitex Company.
Hidalgo	*La Blanca	Gas/Dist	3	6650–8000	None	Atlantic, Phillips, Quintana, Davenport, etc.
	*Mestina	Gas/Dist	2	6600–8000	None	Gulf States, Union Sulphur, etc.
	*McAllen	Gas/Dist	3	5900–7200	None	Phillips, R. E. Harding.
	*Mercedes	Gas/Dist	8	7400–9000	None	Union Sulphur Co.
	*Samfordyce	Crude/Dist	1	5850	None	Phillips, in distillate area.
	*Weslaco	Gas/Dist	8	6800–9000	None	Atlantic.
Jackson	*Francitas	Crude/Dist	2	7200–7700	None	Texas, Skelly, Ohio, etc.
	*Edna	Gas/Dist	3	4600–5000	None	Chicago Gulf, Steinberger Oil Corp.
Jim Wells	*, †Alice	Crude/Dist	4	4500–5400	None	H. H. Howell, Southern Minerals, R. B. Bryant, etc.
	*E. Prement	Crude/Dist	4	5300–6650	None	Magnolia, Transwestern, etc.
	*E. La Gloria	Crude/Dist	2	7300–7550	None	Shell.
	*Bandera	Gas/Dist	1	6400	None	Magnolia.
	*W. La Gloria	Gas/Dist	6	5200–6200	None	Magnolia.
Kleberg	*Bird Islands	Gas/Dist	1	7200–7300	None	Pure, Superior, etc.
Live Oak	†Lucas	Gas/Crude	...	.....	None	Houston, etc.
	†Dinere	Gas/Crude	...	.....	None	Houston, Smith & Storey, etc.
Nueces	*Agua Dulce	Gas/Dist	6	4600–6300	3	Union Prod., Lockhart, Shelton, etc.
	*Bentonville	Gas/Crude	1	4000	None	La Jita, Stanolind, Lucey, etc.
	*, †Clara Driscoll	Crude/Dist	4	5100–5400	None	Wellington, Pan American, Reed, etc.
	†Luby	Gas/Crude	...	.....	1	Stanolind, Seaboard, Shell, etc.
	*London	Crude/Dist	2	4750–4900	None	Wellington, Atlantic, etc.
	*Riverside	Gas	...	.....	None	Stanolind, Seaboard, Shell, etc.
	†Flower Bluff	Crude	...	.....	1	Humble, Barnsdall.
	*, †Saxet	Gas/Dist./Crude	12	4800–10000	1	Southern Minerals, Heep, Richardson, Texon, etc.
	*Stratton	Gas/Dist	5	4700–6600	1	Corpus Christi Corporation.
	*S. Agua Dulce	Gas/Dist	3	5800–6800	None	Texon, Lockhart, etc.
	*N. Agua Dulce	Gas/Dist	1	4700	None	Union Producing, etc.
Refugio	*, †La Rosa	Crude/Dist	1	5400	None	Geophysical Service, Inc., etc.
	*, †Refugio	Crude/Dist	9	5100–7200	2	Republic Nat. Gas, Union, Houston.
	*, †Tom O'Connor-Greta	Crude/Dist	3	5100–5600	None	Quintana, Humble Copano.
San Patricio	†Sinton	Gas/Crude	...	.....	None	Hewitt & Doughtery, Plymouth, etc.
	†Plymouth	Gas/Crude	...	.....	1	Plymouth, Heep, Magnolia, etc.
	†E. White Point	Crude	...	.....	None	Plymouth, Texas, Shell, etc.
Starr	*Rincon	Gas/Dist	1	4700	None	Transwestern Oil Company.
	†Sun	Gas/Crude	...	.....	None	Sun, Magnolia, etc.
Victoria	*Placedo	Crude/Dist	2	5300–5500	None	Barnsdall, Sun Magnolia, etc.
	†Keeran	Crude/Dist	3	5100–7000	None	Union Oil Co., Gulf, Barnsdall.
	†E. Placedo	Gas/Crude	...	.....	None	Stanolind.
Willacy	*La Sal Vieja	Gas/Dist	1	7500	None	Shell.

* Fields considered adaptable to recycling. † Crude producing areas in which gas may be processed.

Hydration of Olefins

The action of aqueous solutions of sulfuric acid on propylene in the presence of highly active catalysts

V. S. GUTYRYA and V. L. BUINITSKAYA

Translated from *Azerbaidzhanskoe Neftyanoe Khozyaistvo*, 1937, No. 1, 50-58, by A. A. Boehtlingk, 2022 Cedar Street, Berkeley, California*

THE crude propylene used in the tests was obtained by the "pyrolysis of petroleum products" and contained about 8 percent (by volume) of propylene. This was concentrated to about 25 to 30 percent of propylene (by volume) by condensing the condensable fraction at low temperature or by fractionation with activated carbon. The concentrated propylene fraction was then treated in a mechanically-driven reactor with 84 percent sulfuric acid at 20° C. and atmospheric pressure. The mixture of isopropylsulfuric acid and polymers thus produced was diluted with 3 to 4 volumes of ice water and allowed to stand for two days. The polymers were then separated and the aqueous solution of the isopropylsulfuric acid was hydrolyzed and distilled. The resulting isopropyl alcohol was neutralized with potassium hydroxide, salted out with sodium chloride, and fractionally distilled through a tower containing metallic spirals. The fraction boiling at 81-83° C. had a specific gravity of 0.8229 at 15° C., corresponding to a 87 percent (by weight) content of pure isopropyl alcohol. This was then subjected to dehydration by passing over aluminum hydroxide at 350° C., resulting in a 90-100 percent pure propylene, which was used in the following tests.

APPARATUS

The reaction was carried out in a horizontal agitator or contactor, 200 mm. long by 65 mm. in diameter. A central shaft, mounted on ball bearings and carrying a series of paddles, was rotated at 100 r.p.m. and had a clearance between the ends of the paddles and inner wall of contactor of 1 to 1.5 mm. Charging and removal of materials were through ¼-inch pipes. Temperature control was effected by passing cold water through cooling coils mounted on the inside of the contactor and by electrically-heated coils of resistance wire mounted on the outside.

(*This abstract is submitted by the Petroleum Division of the American Chemical Society, which, however, assumes no responsibility for the facts and opinions presented in this paper, nor does it necessarily endorse statements made in it.)

PROCEDURE

The propylene from a calibrated, 16-liter glass bottle-type gasometer was measured by an orifice flowmeter and passed at a constant rate into the reaction vessel containing the sulfuric acid. The unreacted gas was passed through a series of water-cooled condensers and measured in a second gasometer.

The mixture of isopropylsulfuric acid and unreacted sulfuric acid from the reaction chamber was mixed with 3 to 4 times its weight of finely cracked ice and then heated to boiling. The isopropyl alcohol which distilled off was collected in 100-50 cc. fractions, the specific gravity of each fraction was determined by means of a picnometer or Westphal balance and the alcohol content calculated by means of the tables taken from "Manual of Technical Encyclopedia (Spravochnik tekhnicheskoi entsiklopedii). After they had been separated from the sulfuric acid mixture by the addition of the water, the quantities (if any) of the polymers formed were measured.

The operating conditions were:

Velocity of propylene through apparatus	1.0 liters per hr.
Contact time	1 to 6 minutes
Sulfuric acid used (Corresponding to 38 to 45 gms. of the monohydrate.)	60 to 65 gms.
Propylene purity	88 to 99 percent
Propylene used (Calculated to correspond with the theoretical amount of propylene required for the conversion of the 38-45 gms. of the monohydrate into isopropyl sulfuric acid.)	18 to 22 gms.

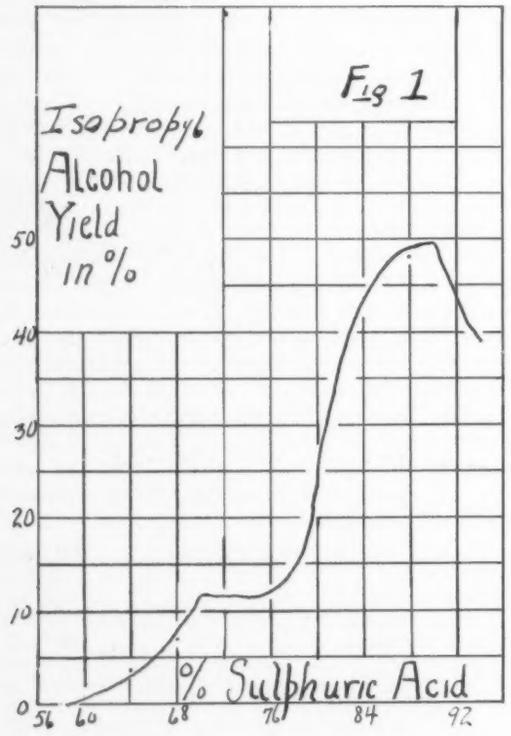
In the first series of experiments the influence of the concentration of the acid on the reaction between propylene and sulfuric acid was investigated over the range of 58 to 94 percent sulfuric acid in 2 percent increments. Results are given in Table 1.

From the results it was concluded that (1) the yield of alcohol decreased with increased polymerization of propylene over the range 90 to 94 percent sulfuric acid, (2) polymerization of propylene decreased slowly over the range, 90 to 80 percent sulfuric acid, practically ceasing with the 80 percent acid, (3) with lower concentration of acid, i.e. down

TABLE 1

Concn. H_2SO_4	G. Acid on Monohydrate	Percent C_3H_6 in Gas	Amt. C_3H_6 Gr.	Mean Temp. ° C.	ALCOHOL YIELD IN		Percent Conversion of C_3H_6 into Alcohol	Amt. Polymers in Cc.
					Grams	Percent Monohydrate		
94.0	47.0	99.0	19.2	32	18.5	39.3	64.7	3.1
92.0	46.0	99.0	19.0	31	19.7	42.8	72.8	1.2
90.0	45.0	97.0	20.7	34	22.3	49.5	75.4	0.8
88.0	44.0	95.0	20.3	30	20.2	45.9	70.0	0.4
86.0	43.0	97.0	20.3	32	19.7	45.8	68.0	0.3
84.0	42.0	97.0	20.1	34	17.8	42.4	62.0	0.2
82.0	45.1	97.0	19.0	35	15.9	35.4	56.4	...
80.0	44.0	97.0	19.7	34	9.8	22.3	34.8	Traces
78.0	42.9	97.0	18.8	36	7.8	18.2	29.0	None
76.0	41.8	92.0	19.5	34	5.2	12.4	18.6	None
74.0	40.7	97.4	19.0	37	4.8	11.8	17.6	None
72.0	39.6	97.0	19.8	35	4.6	11.6	16.4	None
70.0	38.5	97.0	19.7	35	4.4	11.4	15.7	None
68.0	40.8	97.0	20.0	33	2.8	7.0	10.0	None
66.0	39.6	97.0	20.0	36	2.0	5.0	7.0	None
64.0	38.4	97.0	20.0	36	1.4	3.6	4.8	None
62.0	40.3	93.0	18.0	35	0.6	1.5	2.3	None
60.0	39.0	93.0	18.3	35	0.4	1.0	1.5	None
58.0	37.7	93.0	19.0	33	0.0	0.0	0.0	None

to 58 percent, the alcohol yield decreased with decrease in acid concentration, and (4) the peculiar break in the curve (see Figure 1) corresponding to acid concentrations of 70 to 76 percent is due to unsaturation of the acid by the propylene. Additional tests, in which saturation had been effected, resulted in a somewhat smoother curve.



EFFECT OF CATALYSTS

The results of a series of tests on the effects of catalysts are given in Tables 2 to 6.

The catalysts seemed only to increase the rate of conversion of the propylene in the earlier phases of the reaction, the entire system soon approaching the equilibrium which was approached without the use of catalysts. The best catalyst was silver sulfate, which increased the yield somewhat, but was effective only in those cases in which the acid had not been saturated with propylene. This increased con-

TABLE 2

45.1 grams of 82 percent acid, calculated on monohydrate were taken in each experiment

Catalyst		C_3H_6 Concn. in Gas	Grams C_3H_6	Temp. in ° C.	Alcohol Yield In		Percent C_3H_6 Convtd. to Alcohol
Composition	Percent on H_2SO_4				Grams	Percent Monohydrate	
None.....	None	97.0	19.0	35	15.9	35.4	56.4
$CuSO_4$....	2.5	95.0	18.7	34	15.2	33.8	56.4
H_3PO_4....	8.5	99.0	19.3	36	15.7	34.9	56.9
Ag_2SO_4....	2.5	97.6	19.0	34	20.7	46.0	76.3

TABLE 3

41.8 grams of 76 percent acid, calculated on the monohydrate were taken in each experiment

Catalyst		C_3H_6 Concn. in Gas	Grams C_3H_6	Temp. in ° C.	Alcohol Yield In		Percent C_3H_6 Convtd. to Alcohol
Composition	Percent on H_2SO_4				Grams	Percent Monohydrate	
None.....	None	92.0	19.5	34	5.2	12.4	18.6
H_3PO_4....	8.5	90.0	17.8	36	5.3	12.6	20.8
Ag_2SO_4....	2.5	95.3	18.8	36	17.0	40.7	63.3

TABLE 4

38.5 grams of 70 percent acid, calculated on the monohydrate, were taken in each experiment

Catalyst		C_3H_6 Concn. in Gas	Grams C_3H_6	Temp. in ° C.	Alcohol Yield In		Percent C_3H_6 Convtd. to Alcohol
Composition	Percent on H_2SO_4				Grams	Percent Monohydrate	
None.....	None	97.0	19.7	35	4.4	11.4	15.7
$CuSO_4$....	2.5	98.4	19.0	32	4.1	10.6	15.1
H_3PO_4....	8.5	96.5	20.0	37	4.9	12.7	17.1
Ag_2SO_4....	2.5	97.4	18.7	36	7.4	17.7	27.7

TABLE 5

38.4 grams of 64 percent acid, calculated on the monohydrate, were taken in each experiment

Catalyst		C_3H_6 Concn. in Gas	Grams C_3H_6	Temp. in ° C.	Alcohol Yield In		Percent C_3H_6 Convtd. to Alcohol
Composition	Percent on H_2SO_4				Grams	Percent Monohydrate	
None.....	None	97.0	20.0	36	1.40	3.6	4.8
$CuSO_4$....	2.5	97.0	18.6	35	1.00	2.6	3.8
H_3PO_4....	8.5	97.0	18.3	37	1.45	3.7	5.5
Ag_2SO_4....	2.5	96.0	18.4	36	1.45	3.7	5.5

TABLE 6

37.7 grams of 58 percent sulfuric acid, calculated on the monohydrate, were taken in each experiment

Catalyst		C_3H_6 Concn. in Gas	Grams C_3H_6	Temp. in ° C.	Alcohol Yield In		Percent C_3H_6 Convtd. to Alcohol
Composition	Percent on H_2SO_4				Grams	Percent Monohydrate	
None.....	None	93.0	19.0	33	0.0	0.0	0.0
Ag_2SO_4....	2.5	92.5	16.2	37	0.8	0.8	1.3

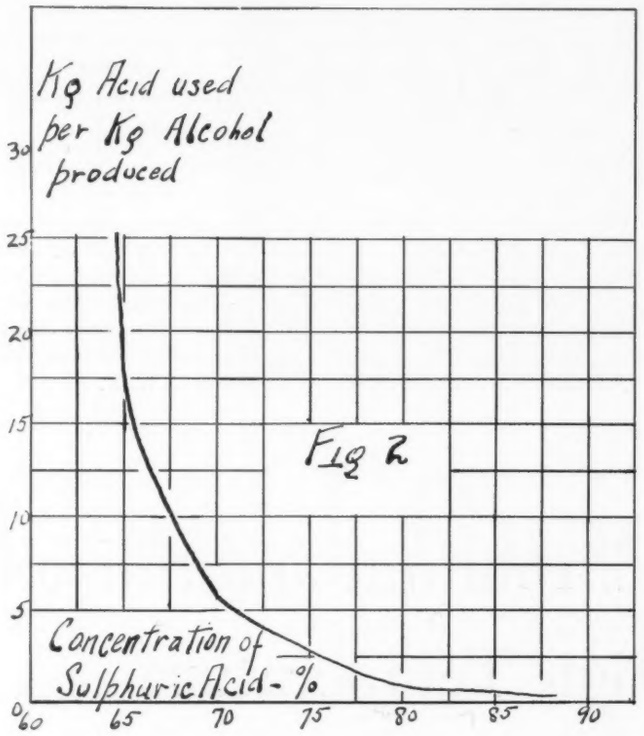
TABLE 7

Concentration of Acid	Alcohol Yield in Percent on the H_2SO_4	Consumption of H_2SO_4 in Kg. per Kg. of Alcohol
88.5.....	70.5	1.42
85.7.....	66.5	1.50
83.1.....	63.0	1.58
82.0.....	55.5	1.80
79.7.....	56.5	1.76
77.2.....	36.0	2.78
76.0.....	37.8	2.64
70.0.....	16.7	6.08
64.0.....	3.9	25.60

version was ascribed to the auto-catalytic action of isopropyl sulfuric acid.

At the beginning of the reaction isopropyl sulfuric acid is formed slowly and little propylene is consumed. After this the reaction speeds up, attains a maximum and then slows down. In the case of 70 percent acid the maximum absorption of propylene occurs when 20 to 40 gms. of propylene have passed through the acid. With the 70 percent acid the maximum absorption coincides with the beginning of the upward trend of the propylene absorption curve for the 76 percent acid.

The data are summarized in Table 7 and Figure 2.



From the data a hyperbola of the form, (x—63.3) (y—0.85) = 15.5, may be obtained. This would indicate that for acids less concentrated than 63 percent sulfuric acid no reaction is possible; also that the point 0.85 should correspond to the theoretical consumption of sulfuric acid per kilogram of isopropyl alcohol produced.

THE EFFECT OF TEMPERATURE

The effect of temperature on the reaction is given in Tables 8 to 11 and is presented graphically in Figure 3.

With increase in temperature a slow increase followed by an accelerated increase in alcohol yield was observed in those cases in which the acid had not been saturated with propylene.

TABLE 8

45.1 grams of 82 percent acid, calculated on the monohydrate, were used in each experiment

Mean Experim. Temp.	Concn. of C_3H_6 in the Gas	Amount of C_3H_6 in Grams	Alcohol Yield In		Percent Converted C_3H_6	Amount of Polymers in Cc.
			Grams	Percent Monohydrate		
34	97.0	19.0	15.9	35.4	56.4	0.2
50	97.4	21.8	17.7	39.3	56.8	0.3
60	90.0	19.8	19.7	43.8	70.0	0.7

TABLE 9

41.8 grams of 76 percent acid, calculated on the monohydrate, were used in each experiment

Mean Experim. Temp.	Concn. of C_3H_6 in the Gas	Amount of C_3H_6 in Grams	Alcohol Yield In		Percent Converted C_3H_6	Amount of Polymers in Cc.
			Grams	Percent Monohydrate		
34	90.0	9.1	2.0	4.8	15.4	None
50	90.8	8.7	3.0	7.1	24.1	Traces
68	90.8	9.3	6.5	15.5	48.9	0.3

TABLE 10

38.5 grams of 70 percent acid, calculated on the monohydrate, were used in each experiment

Mean Experim. Temp.	Concn. of C_3H_6 in the Gas	Amount of C_3H_6 in Grams	Alcohol Yield In		Percent Converted C_3H_6	Amount of Polymers in Cc.
			Grams	Percent Monohydrate		
31	90.0	8.8	1.00	2.6	8.0	None
54	89.0	9.1	1.90	4.9	14.6	None
68	91.0	9.0	3.30	8.6	25.6	Traces

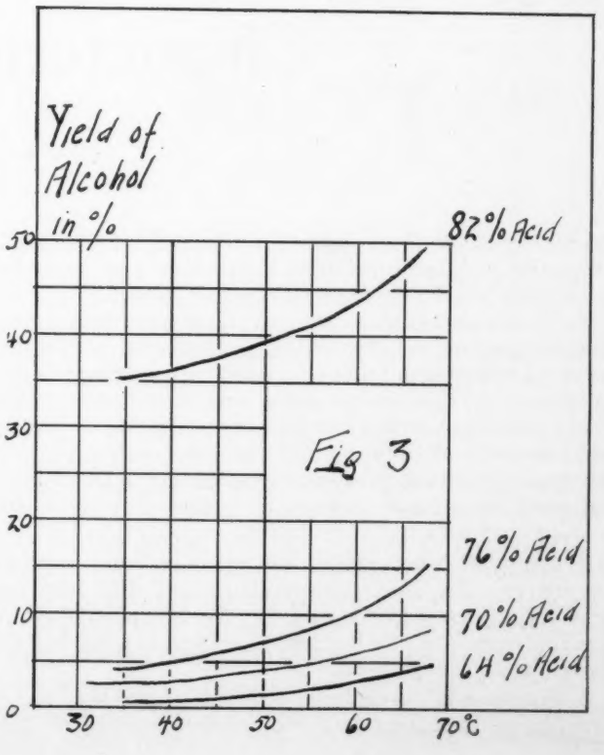
TABLE 11

38.4 grams of 64 percent acid, calculated on the monohydrate, were used in each experiment

Mean Experim. Temp.	Concn. of C_3H_6 in the Gas	Amount of C_3H_6 in Grams	Alcohol Yield In		Percent Converted C_3H_6	Amount of Polymers in Cc.
			Grams	Percent Monohydrate		
35	90.0	9.3	0.25	0.6	1.8	None
52	89.0	8.7	0.60	1.6	4.8	None
68	91.0	9.5	1.95	5.0	14.3	None

ESTER FORMATION

Ester formation was studied by mixing weighed samples of acid of definite concentration with weighed samples of the isopropyl alcohol, maintaining them at room temperature and then titrating



with tenth normal potassium hydroxide. The difference between the quantity of hydroxide required by the acid and that required by the mixture of the acid and the alcohol was used as an index of the extent to which reaction had taken place. Data obtained with solutions maintained at 25° to 32° C. for 80 hours are given in Tables 12 and 13.

TABLE 12

Grams of Acid	Amount of Monohydrate in Acid	Concentration of Acid in Percent	G. of Absol. Alcohol	Percent C_3H_7OH on Monohydrate
6.1807	3.1070	50.27	2.0887	67.2
5.7972	3.2354	55.81	2.0816	64.4
6.1768	3.8114	61.70	2.0860	54.8
6.5243	4.3751	67.06	2.0973	48.0
6.7869	5.3634	79.02	2.0723	38.6

TABLE 13

H_2SO_4 Concn.	Amount of KOH in G.			H_2SO_4 Conversion into $C_3H_7OSO_3H$	
	Required	Used	Lowering	In Grams	In Percent
50.27	3.5550	3.5446	0.0104	0.0182	0.58
55.81	3.7020	3.6890	0.0130	0.0227	0.70
61.70	4.3610	4.2472	0.1138	0.1989	5.22
67.06	5.0060	4.7954	0.2106	0.3681	8.41
79.02	6.1370	5.6517	0.4853	0.8482	15.81

Further tests run at boiling water temperature for one hour, using sealed ampoules, indicated that with mixtures of 79 percent sulfuric acid and isopropyl alcohol, the equilibrium is reached just as rapidly at the higher temperature as at room temperature. However, with more dilute acids ester formation seemed to increase somewhat with heating; some reaction was even noticeable in the case of 50 percent sulfuric acid at 100° C.

EFFECT OF ALKALI METAL SALTS

The hydrolysis of isopropyl sulfuric acid by alkali metal salts in dilute solution was studied by titrating with alkali the sulfuric acid which had been used to absorb the propylene. Data are given in Table 14.

TABLE 14

H_2SO_4 Concn.	Amount of H_2SO_4 in Grams	C_3H_6 Concn. in Gas	Amount of C_3H_6 in Grams	Temp. in ° C.	G. Alcohol Yield	
					Hydrolysis	Titration
59.2	38.5	90.6	9.4	74	0.6	0.7
65.6	42.6	90.6	9.5	73	1.3	1.2

The data indicate that hydration of propylene does not occur at temperatures below 70° to 75° C. and that a stable isopropyl sulfuric acid is formed under the conditions of test. They also indicate that increasing the temperature of reaction tends to shift the theoretical limits for the reaction somewhat in the direction of lower concentration of acid.

Influence of Varying Chromium and Silicon Content on the High Temperature Characteristics of Steel

(*Continued from Page 72*)

chromium and silicon content on each of the high-temperature characteristics. Certain of the more definite effects may be summarized as follows:

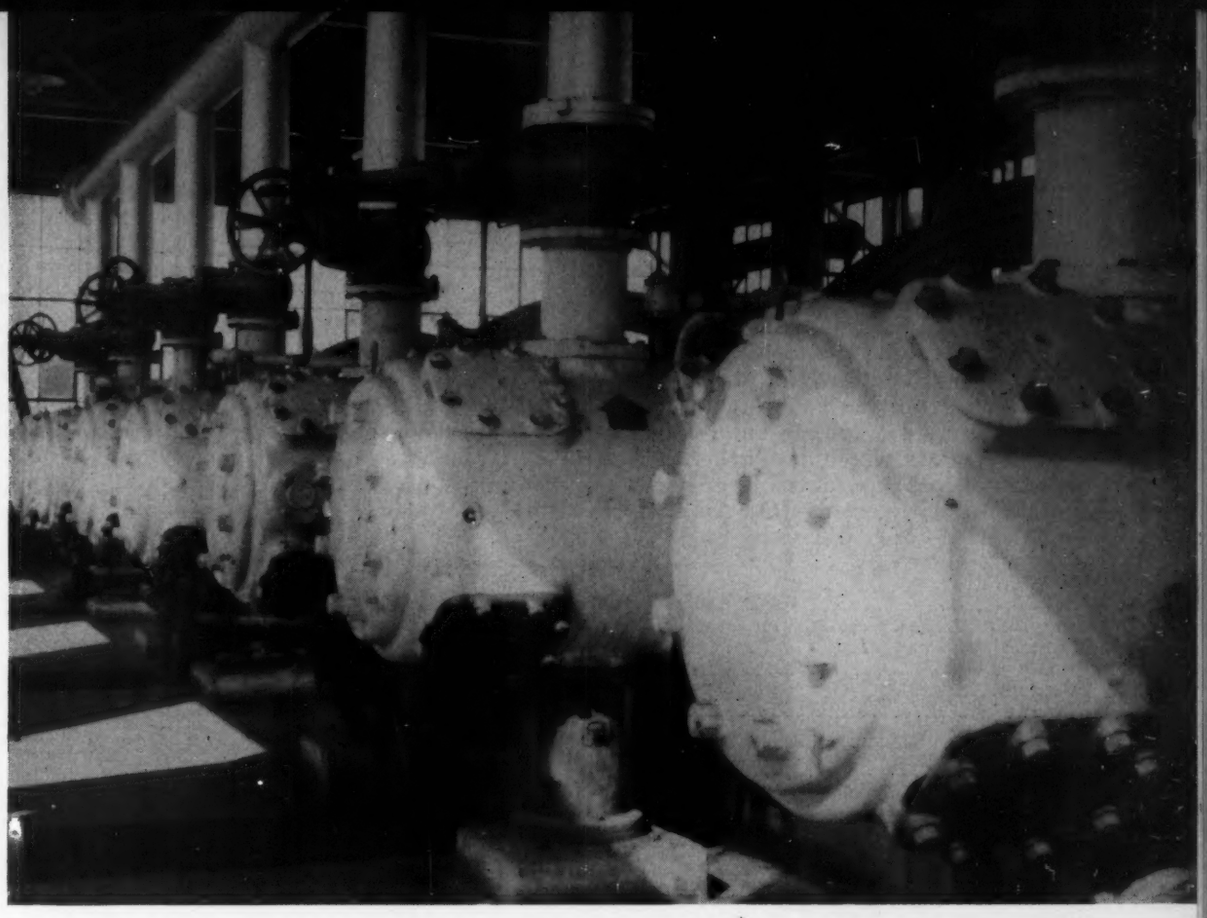
1. Increased silicon content over the range considered and especially in the presence of chromium increases the (a) room-temperature strength and hardness, (b) the short-time strength at 750 and 900° F., (c) the hot impact resistance, (d) the oxidation and corrosion resistance, (e) the rupture strength at the more elevated temperatures, and (f) the life of the steel in service, especially because of increased surface and structural stability.

2. On the other hand, increased silicon content lowers (a) the room-temperature ductility and impact resistance slightly, and (b) the creep strength at the intermediate temperatures, especially under the more rapid creep rates.

3. Increased chromium content over the range considered increases (a) the room-temperature ductility and impact resistance, (b) the corrosion resistance, (c) the oxidation resistance at the intermediate temperatures, and (d) the short-time high-temperature strength and creep resistance in amounts up to 1.0 to 1.5 percent chromium. Insofar as the rupture strength and hot impact resistance is concerned, the effect of chromium varies, depending on the temperature and the silicon content.

4. The results presented are believed to definitely show that very satisfactory steels for high-temperature service can be obtained through a proper combination of chromium and silicon in the presence of 0.50 percent molybdenum.

5. While some may feel the number of steels considered to be excessive, it is believed that each is capable of rendering satisfactory service under certain conditions and that a wide choice must be available if the most economical steel is to be chosen for each application.



Interior of compression plant, Wilmington Gasoline Company, Terminal Island plant, Wilmington, Calif.

Good Efficiency At Low Load

IN WILMINGTON PLANT

AFTER drilling had been carried to such an extent that many large wells were indicated for Terminal Island, located both in the cities of Los Angeles and Long Beach, California, plans were consummated that resulted in the building of a gasoline plant in that area. Municipal restrictions prevented operation of additional gasoline plants within the corporate limits of Long Beach, which made it necessary to select a site just inside the city of Los Angeles, some distance from existing oil wells, but within potential producing area.

The plant was reconditioned from a shut-down unit no longer required at Signal Hill, which was torn down and moved by truck to the new site. The original plant was in good condition, including gas engine-driven compressors, absorbers, distillation apparatus and the like, but was rearranged by Fluor Construction Company, who moved the machinery and rebuilt the plant for Wilmington Gasoline Company.

The engines, originally with 16 x 20-inch power cylinders, were equipped with 17 x 20-inch cylinders, fitted with overhead exhaust and gas injection cylinder heads and timing apparatus. As the ground upon which this plant was built consists of dredgings from the channels and ship basins nearby, it required subsurface reinforcing by driving numerous wood piles to firm formation several feet below the surface, upon which the foundations and engine-room mat were poured. Likewise, all columns and other heavy equipment, were furnished with pile-reinforced foundations to miminize vibration.

The wells from which the gas is obtained are mostly located on the eastern end of the island, and the rich gas from separators and flow tank batteries is transported through a 20-inch pipe line, laying above ground on blocks and concrete piers. The salty condition of this soil, together with the shallow water table causes corrosion to attack pipe unless

protected with several layers of effective coating, which is more expensive than maintaining the system above ground level. To return stripped residue gas to the wells for operation, and to furnish fuel for drilling additional wells, a 16-inch asphalt primed pipe line was laid.

The capacity of the plant is calculated as 20,000,000 cubic feet, having a distillation capacity of 30,000 gallons of finished gasoline daily. Due to restricted production of oil the gas volume is also reduced to approximately 4½ million cubic feet daily. The gas from the sands which produce the oil (three have been discovered) contains a large portion of methane, and almost 5 percent of CO_2. An analysis of the gas is shown below:

Fraction	Percent by Volume	Gasoline Content
Air	0.50	
CO_2	4.90	
Methane	71.59	
Ethane	7.37	
Propane	7.54	2.05
i-Butane	1.26	0.41
n-Butane	3.43	1.03
Pentane plus	3.41	1.34
Totals	100.00	4.88

Because of the enforced reduction in gas volume from the field, the amount of gas processed is only about 16 percent of the plant capacity, which is detrimental to the over-all yield of finished gasoline. While it is possible to extract a large amount of lower-boiling fractions with the desirable hydrocarbons, the process of finishing the material to marketable gasoline results in over fractionating the raw gasoline.

One of the interesting features of this plant is the almost entire condensation of exhaust steam, which is returned as condensate to the boiler water supply.

Temperatures of the raw gas, and the temperatures of the lean oil pumped to the absorber are low; the first averaging 62° F., and the second 70° F. These temperatures are obtained by the operation of a new type cooling tower, designed for low wind velocity and a high rate of heat extraction.

Another feature of the plant is one which is becoming more in general practice than formerly and is that of cooling engine jackets with water from which all scale-forming solids have been removed, and carrying this water in a closed circuit. The water for engine-jacket cooling is handled by small automobile engines, adapted for pump drive by changing the original crankcase for a special base which contains a greater amount of lubrication, and also permits installation upon a concrete foundation, instead of special supports front and rear.

As market requirements keep the plant under control, so far as finished product is concerned, a greater amount of gasoline could be finished if the vapor pressure could be raised. The following analyses indicate the condition of both raw and finished 21-pound Reid gasoline:

Fraction	Raw Gasoline Mol Percent	Finished Gasoline Mol Percent
Methane	0.1	Nil
Ethane	0.5	Nil
Propane	7.4	Nil
i-Butane	8.0	0.3
n-Butane	39.2	29.8
Pentane plus	44.8	69.9
Totals	100.0	100.0

To obtain this product, the raw gasoline is fractionated with a stabilizer pressure of 175 pounds, gauge; a kettle temperature of 268° F., and a top temperature of between 120 and 125° F. In the overall operation, the plant—on August 24, 1938—processed 4,563,000 cubic feet of wet gas, and metered 4,286,000 cubic feet of residue gas, a shrinkage of 277,000 cubic feet, which resulted in a finished product of 7,928 gallons of 21-pound gasoline.

The accompanying fractional analyses of wet gas, dry gas, raw gasoline to the stabilizer and finished gasoline from the stabilizer were prepared by and are presented here through the assistance of Edgar E. Shafer, Jr., of Wilmington Gasoline Company.

Fractional analyses of Wet Gas and Plant Intake. Sample taken August 24, 1938.

Fraction	Percent by Volume	Gasoline Content Gal. Per Mcf.
Air	0.50	
Carbon Dioxide	4.90	
Methane	71.59	
Ethane	7.37	
Propane	7.54	2.05@
i-Butane	1.26	0.41
n-Butane	3.43	1.08
Pentane Plus*	3.41	1.34
Total	100.00	2.83
		@2.05
		4.88

Calculated Specific Gravity: (Air @ 1).....0.860
*Vapor pressure equivalent of Pentanes Plus—25.5 c.f./Gal.

Fractional analysis of dry gas from absorber outlet.

Fraction	Percent by Volume	Gasoline Content Gal. Per Mcf.
Air	0.50	
CO_2	5.30	
Methane	77.30	
Ethane	7.89	
Propane	7.47	2.04@
i-Butane	0.67	0.22
n-Butane	0.80	0.25
Pentane Plus*	0.07	0.03
Totals	100.00	0.50
		@2.04
		2.54

Calculated Specific Gravity: (Air @ 1)..... 0.740
Calculated Gross Btu. per Cu. Ft.....1162.000
*Traces of light gasoline fractions calculates as N-Pentane.

Fractional analysis of Raw Gasoline to Stabilizer. Sample taken August 24, 1938.

Fraction	Percent by Liquid Vol.	Mol %	Part. Press. @ 100° F.
Methane	0.08	0.1	4.0
Ethane	0.35	0.5	3.9
Propane	5.78	7.4	13.8
i-Butane	7.47	8.0	5.9
n-Butane	35.38	39.2	20.4
Pentanes-Plus	50.94	44.8	5.2
Totals	100.00	100.00	53.2 lbs. Absolute

A.P.I. Gravity of Pentanes-Plus.....76.9° @ 60° F.
Vapor Pressure of Pentanes-Plus.....11.5 lbs. @ 100° F.

Fractional analysis of Finished Gasoline from Stabilizer. Sample taken August 24, 1938.

Fraction	Percent by Liquid Vol.	Mol %	Part. Press. @ 100° F.
Propane	Nil	Nil	Nil
i-Butane	0.29	0.3	0.2
n-Butane	25.23	29.8	15.5
Pentanes-Plus	74.48	69.9	9.0
Totals	100.00	100.00	23.7 lbs. Absolute

A.P.I. Gravity of Pentanes-Plus Gasoline....76.9° @ 60° F.
Vapor Pressure of Pentanes-Plus Gasoline.11.5 lbs. @ 100° F.

Purification of Absorption Oil In Gasoline Absorption Plants

W. A. STOVER
Petroleum Engineering, Inc.

THE purification, or reconditioning, of absorption oil is usually accomplished by some method of distillation. One of the first methods for reconditioning absorption oil to come into general use was the fire-still unit, Figure 1. The equipment required for an installation of this kind is a small tank mounted in a furnace to serve as a still for evaporating the oil, a condenser for cooling and condensing the overhead vapors, and a receiver for condensate. The more elaborate installations of this type are equipped with some kind of fractionating column, and have controls to make their operation more-or-less automatic.

Another type of unit for reconditioning absorption oil is the vacuum still. This unit consists of a fractionating still, or a column provided with baffles in its uppermost end, and a steam heater coil in its base. The still is provided with a condenser, a condensate receiver, and a steam jet for maintaining a relatively high vacuum on the entire system. Due to the vacuum held on the system, a pump must be provided for pumping the condensate out of the condensate receiver into the plant system if the unit is to operate continuously. (Figure 2.)

There is still another type of unit being used for the reconditioning of absorption oil. This unit is of recent development (patents pending) and possesses certain improvements of interest.

The unit consists of a still, or tank with trays and baffles, and a heater. This unit works in conjunction with the main absorption plant still and requires no auxiliary equipment such as a condenser, a condensate receiver, or a pump. The unit operates at a pressure of a few ounces above that of the main still to which it is connected.

The operation of the unit is illustrated in Figure 3. The agitation steam, which normally enters the absorption plant still, is diverted and passes into the purifying unit where it evaporates the lighter fractions of the absorption oil contained therein. This steam, saturated with oil vapors, then flows into the absorption plant still, performing its stripping action there in the usual way. The heat required to evaporate the lighter fraction of the absorption oil in the purifying unit is supplied by steam in the heater. Raw oil from the plant system is charged automatically to the purifying unit by a liquid level controller. The raw oil stream is usually taken from the rich oil stream just before it enters the rich oil preheater; at this point the oil is relatively hot and is under sufficient pressure to flow into the purifying unit without the aid of a pump.

The unit requires no additional utilities, such as steam or cooling water. It is true that the heater consumes a small quantity of steam, when the purifying unit is operating, however, the quantity of steam consumed in the rich oil preheater is reduced by a quantity equal to that consumed by the heater on the purifying unit. A heat balance will show that the oil purifying unit will add no additional load to the gasoline condensing system or to any other equipment in the plant.

Only a small portion of the plant oil circulation passes through the oil purifying equipment. This amount will average less than 1 percent of the total oil circulation. In a plant having an oil circulation of 400 gallons per minute there would be approximately 2 to 4 gallons per minute passing through the purifying unit.

In addition to improving the absorption efficiency of the lean oil, it has been observed that the purified oil

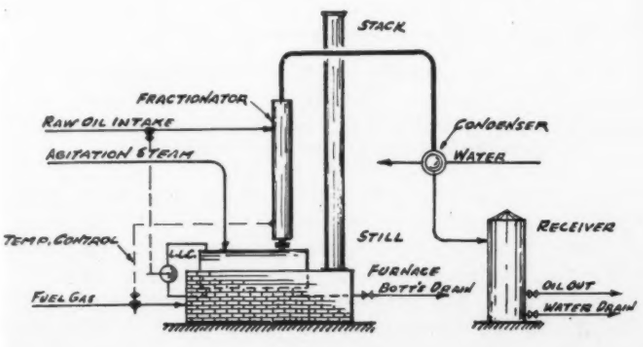


FIGURE 1
Fire Still Oil Rerun Unit.

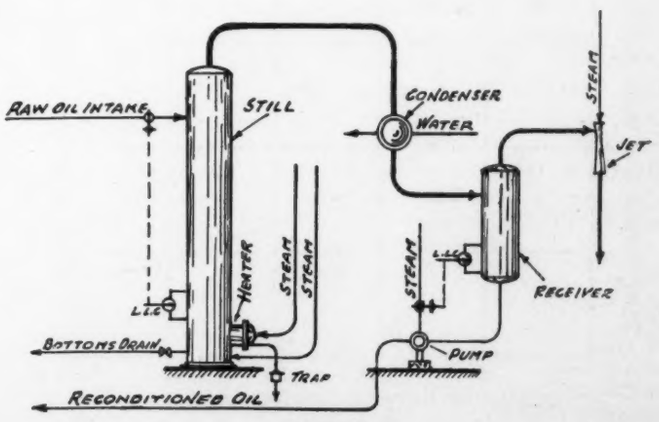


FIGURE 2
Vacuum Still Reconditioning Unit.

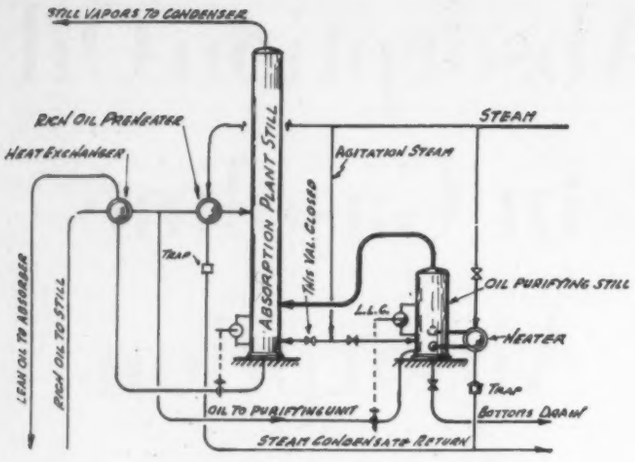


FIGURE 3
Oil Purifying Unit.

removes sediment and gummy deposits from the plant equipment through which it circulates, thus improving operation of the heat exchange equipment and the plant in general.

The accompanying curves will serve to illustrate the performance of the oil purifying unit. These curves were plotted from data obtained from plants in which these units have been installed and they present a clear picture of what should be expected from an absorption oil purifying unit.

Figure 4 shows the increase in efficiency of the lean oil coolers due to the elimination of heavy ends, gummy

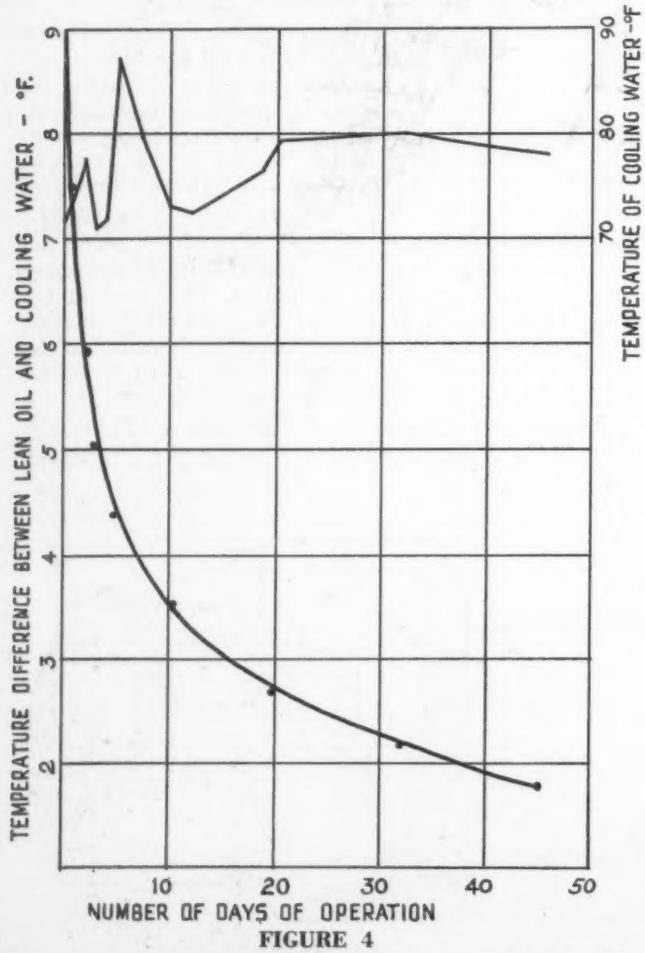


FIGURE 4
Chart showing how the Oil Purifying Unit increased the efficiency of the Lean Oil Coolers during 45 days of operation.

deposits, sediments, etc., from the absorption oil. At the time the oil purifying unit was installed there was a difference of 9° F. between the temperature of the lean oil leaving the oil coolers and the initial temperature of the cooling water. After 45 days of operation with the oil purifying unit this temperature difference was reduced to less than 2° F.

Figure 5 shows how the oil purifying unit decreased the quantity of heavy ends boiling above 525° F. At the time the unit was started 27 percent of the lean oil had a boiling point above 525° F. After 45 days of operation this percentage was reduced to 2 percent. The removal of the heavy ends of an absorption oil improves other characteristics of the oil, such as A.P.I. gravity and molecular weight, which in turn permits a lower oil

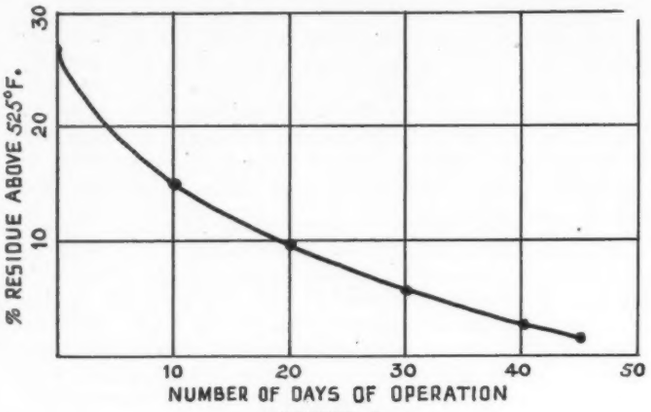


FIGURE 5
Chart showing how the Oil Purifying Unit decreased the end point of the absorption oil during 45 days of operation.

circulation for the same plant efficiency and a consequent reduction in quantity of steam consumed in the distillation process.

Figure 6 shows how the oil purifying unit decreased the gasoline content of plant residue gas. At the time the unit was installed the gasoline content of the plant residue gas was .0549 gallons per thousand cubic feet. After 27 days of operation this quantity was reduced to .0404 G.P.M.

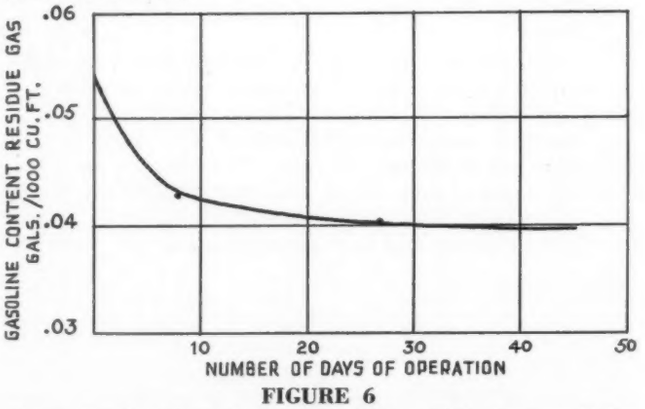


FIGURE 6
Chart showing how the Oil Purifying Unit decreased the gasoline content of the plant residue gas.

In existing plants where units of this type have been installed a decided improvement in plant operating efficiency has been experienced. It has been found that after four to six weeks of operation of this unit the absorption oil has been completely reconditioned and that its quality is equal to that of new oil. It also has been found that no "dumping" of absorption oil is required, thus eliminating quite a sizeable yearly expenditure in some plants.